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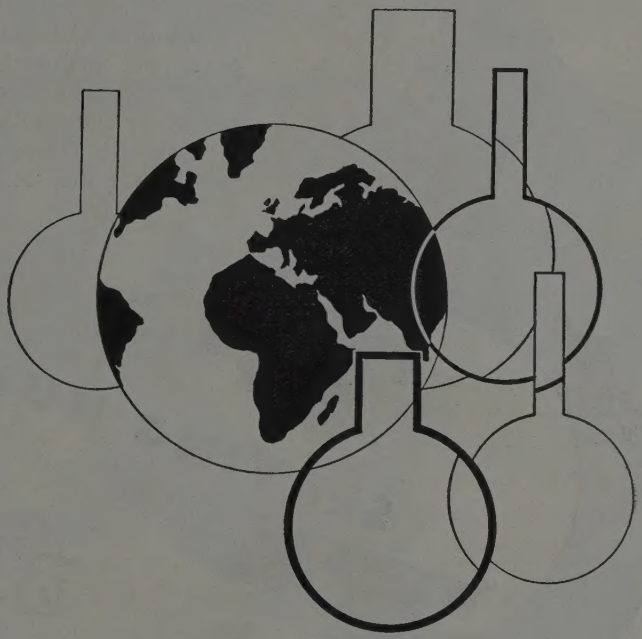

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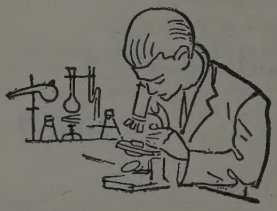

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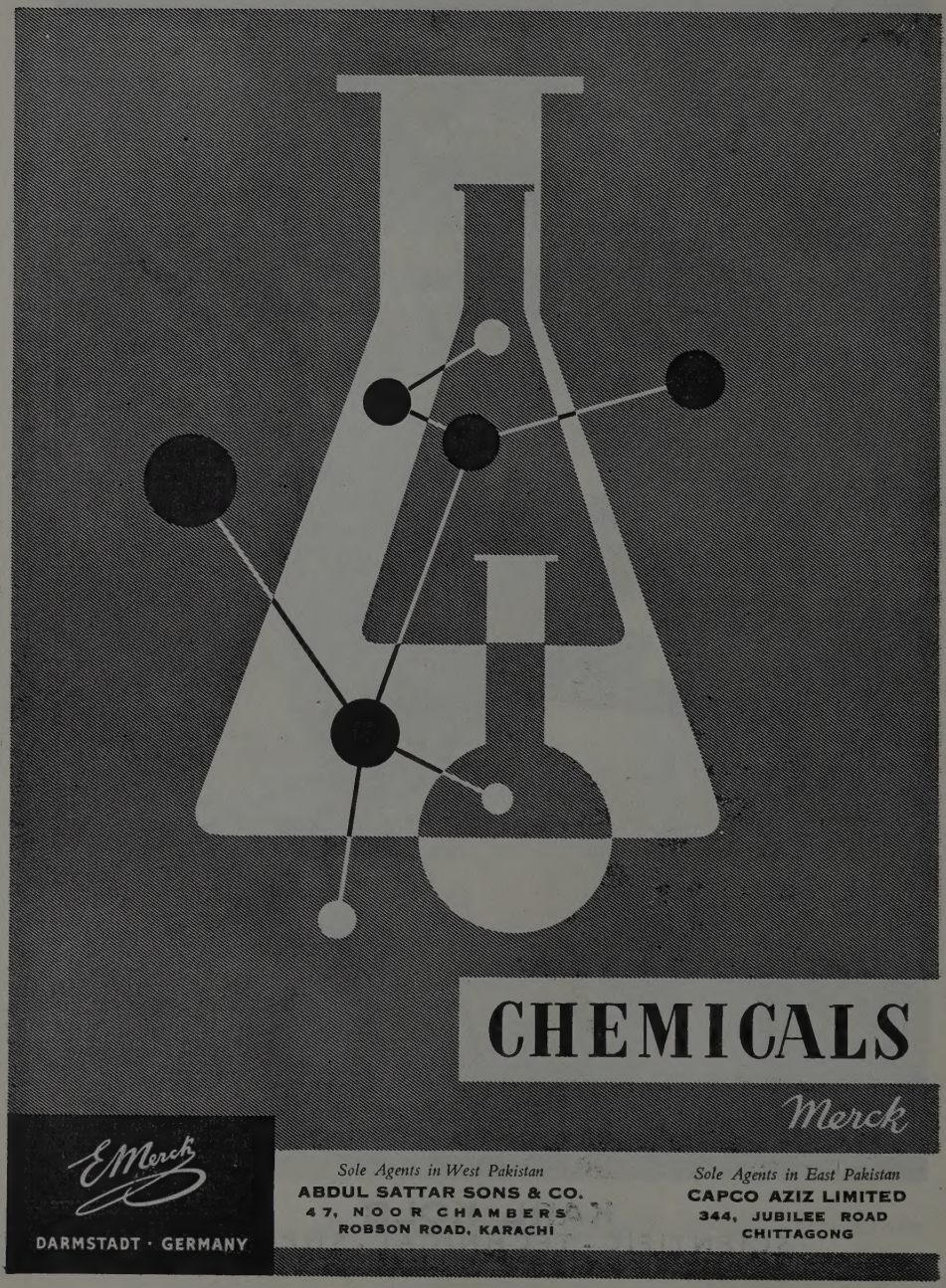

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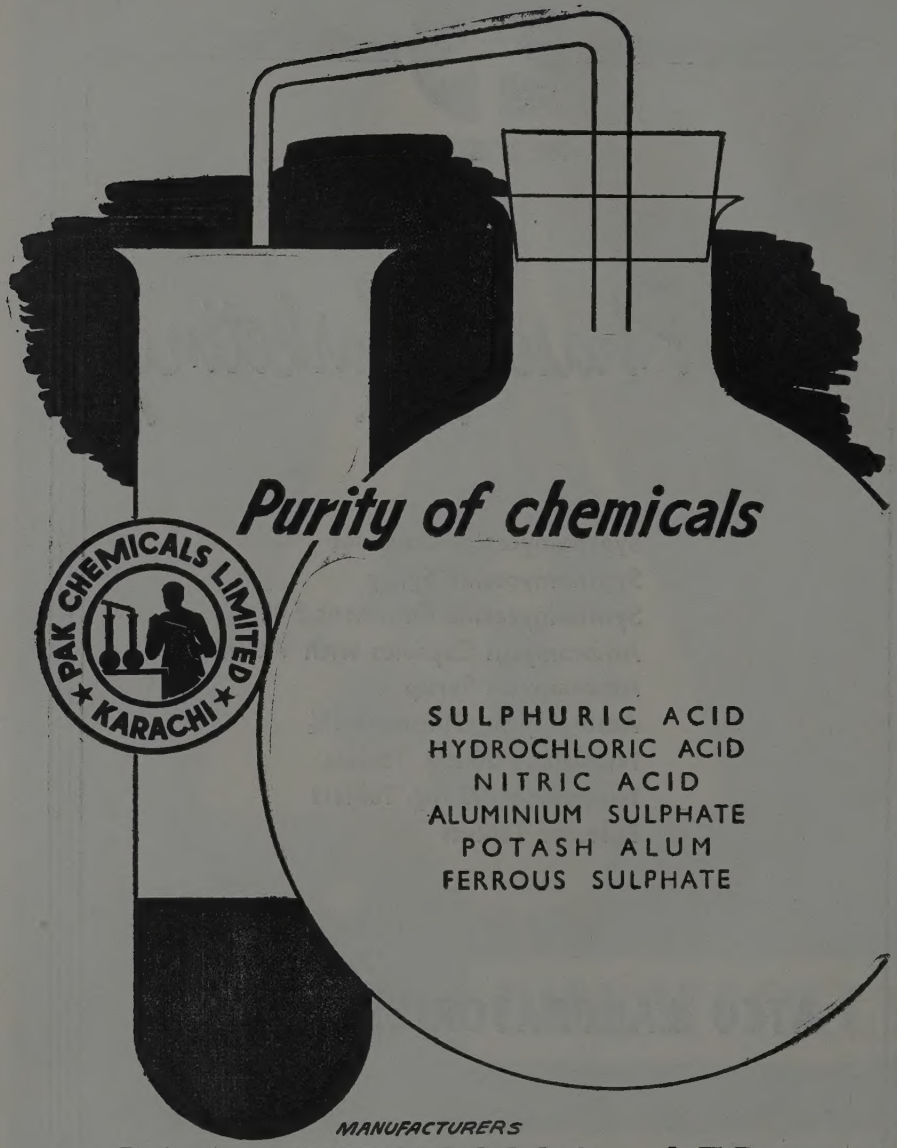

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STUDIES IN THE PROPERTIES OF HEAT INSULATING BUILDING MATERIALS

Part II.—The Thermal Conductivity of Binary Mixtures with Particular Reference to Cellular Concrete

MAZHAR MAHMOOD QURASHI AND A. K. M. AHSANULLAH

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

In Part I of this paper,[1] some measurements were presented on the physical properties of concrete mixtures composed of cement and rice husk ash in various proportions, ranging from 5:1 upto 1:20 by volume. Especially interesting was the curve for thermal conductivity against the composition of the mix, which exhibited an intermediate minimum followed by a maximum, as shown in Fig. 2 in Part I of this paper. It is easily seen that these mixtures essentially form cellular concretes because the ash is extremely porous with a cellular structure (Fig. 6(a) below).

In a system of this type, the thermal conductivity of any particular composition depends on three distinct factors, namely, (1) the law governing the thermal conductivity of a simple mixture of the constituents whithout any changes in volume or chemical interaction, (2) the change in density caused by the purely mechanical volume changes resulting from mixing, setting, etc., and (3) the formation of new products by chemical interaction between the constituents of the mix.

The first factor appears to be the dominant one in the case of concretes of cement and rice husk ash, the second and third coming next in importance. Therefore it was thought advisable first to investigate, both theoretically and experimentally, the thermal conductivities of cellular concretes, and then to apply these results to elucidate the behaviour of the complex cement-rice-husk-ash system, which comprises at least three components, viz., cement, air, and the silica of the ash. In order to analyse the first factor, we must find an accurate expression for the thermal conductivity of intimate mixtures of two substances of thermal conductivities K_a and K_b mixed in various proportions x_a and x_b by volume.

1. Examination of Previous Formulae

Two formulae for the thermal conductivity of porous materials are extant in the literature. The one derived by Russell[2] for rectilinear flow through a cubic array of cubical pores of conductivity K_g embedded in a solid of conductivity K_s gives

$$\frac{K_s}{K} = 1 - P^{1/3} + P^{1/3} \Big/ \left\{ (1 - P^{2/3}) + (K_g/K_s)\, P^{2/3} \right\} \qquad (1a)$$

where the porosity $P = (\rho_s - \rho)/(\rho_s - \rho_g)$.

Since $K_g/K_s << 1$, this makes

$$K \simeq K_g + K_s\,(1 - P^{2/3}).$$

In order to test the applicability of equation 1(a), comparative plots against $(1 - P^{2/3})$ have been made in Fig. 1 for the calculated values (curve I) for cellular concretes and of the standard data (solid circles) given in the literature,[3] K_g being taken as 0.60×10^{-4} cal.cm.$^{-1}$ sec.$^{-1}$/°C. The agreement can only be described as poor, especially

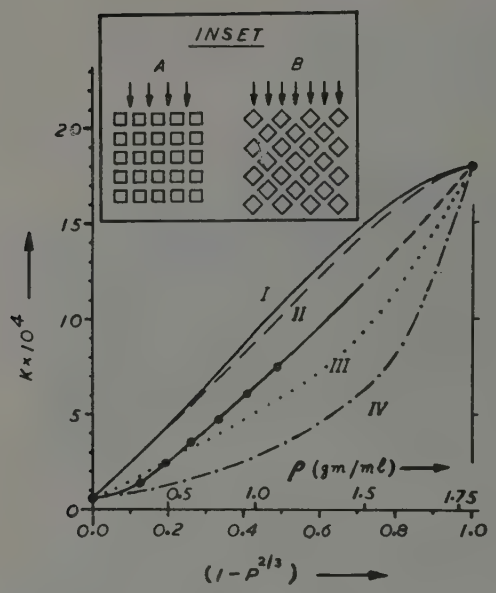

Fig. 1.—Comparative graphs of the thermal conductivity ($K \times 10^4$ cal. cm.$^{-1}$ sec.$^{-1}$/°C.) of cellular concretes against $(1 - P^{2/3})$, where P is the porosity. The solid circles are the experimental points, and the four graphs labelled I to IV are the values calculated on the basis of:

I. Russell's formula for the arrangement 'A' in the inset.
II. Maxwell and Raleigh's formula.
III. Flow along a face-diagonal in Russell's arrangement, as shown at 'B' in the inset.
IV. Flow along a body-diagonal in Russell's arrangement.

at high porosity, and cannot be accounted for by any allowance for the fact that the solid phase is taken as the concrete of density 1.76, which has a porosity of about 0.2. The other equation given in the literature is

$$K/K_s = \left\{1 - (1 - b\,K_g/K_s)P\right\} \Big/ \left\{1 + (b - 1)P\right\} \qquad (1b)$$

with $b = 3\,K_s/(2\,K_s + K_g)$, and was originally derived rigorously by Maxwell[4] and later by Rayleigh[5] for the electrical conductivity of a cubic array of spherical particles in a continuous medium. The values of K obtained from this second formula are shown by the broken curve II in Fig. 1, and give an insignificant improvement on Russell's formula.

The unexpectedly large divergence of the above theoretical formulae from the experimental measurements can be traced to the use of a model with an over-symmetrical arrangement of the pores, thus providing continuous channels of the highly conducting solid medium in directions parallel to the cube edges of the pore lattice as shown at 'A' in the inset to Fig. 1. Moreover, in this highly symmetrical arrangement, very different values are obtained for the conductivity when rectilinear heat flow is considered parallel to the face diagonal of the pore lattice, as shown at 'B' in the inset to Fig. 1. A calculation for this case under the assumptions made in Russell's derivation gives the dotted line curve III, which is in rough agreement with the experimental data. In a similar manner, an approximate calculation for flow along the body diagonal of the lattice gives the lowest (chain-dotted) curve IV, which again deviates markedly from the experimental values.

In view of the above results, it was considered necessary to set up a better model for a homogeneous mixture of two substances, such that the straight continuous channels found in the arrangement discussed above are done away with. Starting with simple composite slabs of the two substances, nearly isotropic blocks can be designed by progressive three-dimensional stacking of the slabs, thus providing a close approach to a homogeneous random mixture of the two components. The principal thermal conductivities are calculated for successive stackings, and a good approach to the ultimate law for a homogeneous mixture is obtained in the third step, this law being in excellent agreement with experimental data.

2. Derivation of the Theoretical Formula for Conductivity of a Simple Homogeneous Mixture

Consider first a composite slab made up of several alternate layers of substance A of thickness δ_a and conductivity K_a, and substance B of thickness δ_b and conductivity K_b (Fig. 2(a)). Such a slab is not isotropic, and its equivalent conductivity, $K_\perp$, for heat flowing perpendicular to the layers (Fig. 2(a)) is different from the equivalent conductivity, $K_{||}$, for heat flowing in the two other principal directions both parallel to the layers (Fig. 2(b)). Figure 2(c) shows schematically the three principal directions for the conductivities, and this presentation indicates that, if several slabs of the type shown in Fig. 2 are stacked together in a three-dimensional array using all the three orientations at random, then, for heat flowing along any one of the principal axes of the array, there will be twice as many slabs in which heat flows parallel to the layers as there are slabs in which the heat flow is perpendicular to the layers. It follows that the resultant conductivity will be a mean of $K_\perp$ and $K_{||}$, weighted in the ratio of

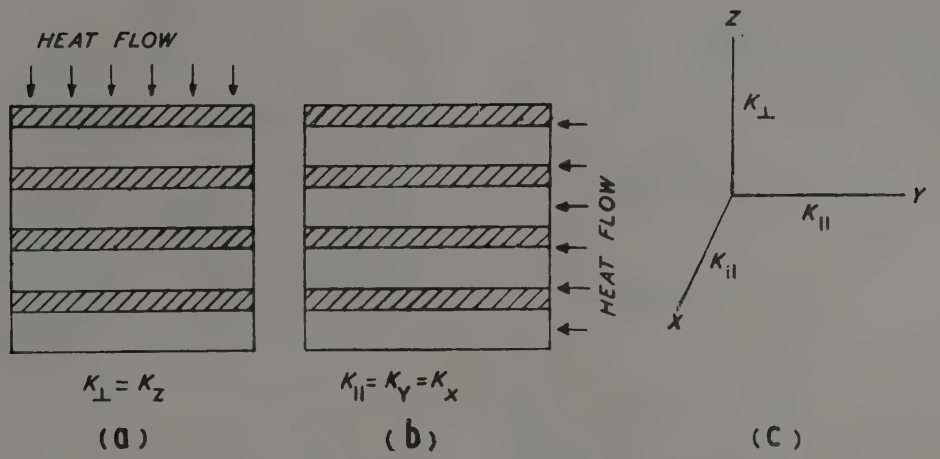

Fig. 2.—Schematic representation of the heat flow in the three principal directions through a composite slab of alternate layers of two materials, A and B: (a) heat flow$_\perp$ layers (b) heat flow$_{||}$ layers (c) the three principal conductivities.

1 to 2. $K_\perp$ and $K_{||}$ are readily calculated and from these values we shall be able to put down the first approximation to the conductivity of an isotropic mixture of the two substances.

$K_\perp$ and $K_{||}$ can be calculated by the usual methods for heat flowing through slabs in series and in parallel (cf. flow of electric current through conductors), and the following formulae are obtained:

$$1/K_\perp = x_a/K_a + x_b/K_b = x_a/K_a + (1 - x_a)/K_b \quad (2a)$$

$$K_{||} = x_a K_a + x_b K_b = x_a K_a + (1 - x_a) K_b. \quad (2b)$$

It is seen that $K_\perp$ is made up of K_a and K_b in harmonic proportion, while $K_{||}$ is made up of K_a and K_b in arithmetic proportion. These formulae for $K_\perp$ and $K_{||}$ can be combined into the general formula,

$$\frac{K^\varepsilon - 1}{\varepsilon} = x_a \frac{K_a^\varepsilon - 1}{\varepsilon} + x_b \frac{K_b^\varepsilon - 1}{\varepsilon}, \quad (3)$$

$K_\perp$ corresponding to $\varepsilon = -1$, and $K_{||}$ to $\varepsilon = +1$. (The term $-1/\varepsilon$ on either side of formula (3) cancels out when $\varepsilon \neq 0$, while for $\varepsilon = 0$ this formula reduces to $\ln K = x_a \ln K_a + x_b \ln K_b$). If now a mean were to be taken of $K_\perp$ and $K_{||}$ with equal weights, it is easily seen that the resultant formula* would closely correspond to (3) with $\varepsilon = 0$ (mean of -1 and $+1$), i.e. to the formula $\ln K = x_a \ln K_a + x_b \ln K_b$, i.e.

$$K = K_a^{x_a} K_b^{x_b} \quad (5)$$

This is the formula for mixing by geometric proportion, and is quite to be expected, because it is well known that the geometric mean of two quantities is also the geometric mean of their arithmetic and harmonic means.

In our case, however, Fig. 2(c) requires that we take the weighted mean with weights of 1 and 2 for $K_\perp$ ($\varepsilon = -1$) and K_{II} ($\varepsilon = +1$), respectively. We may therefore expect that the resultant formula will be a special case of (3) with $\varepsilon = (1/3 \times (-1) + 2/3 \times 1) = 1/3$, i.e.

$$\frac{K_{mix}^{1/3} - 1}{1/3} = x_a \frac{K_a^{1/3} - 1}{1/3} + x_b \frac{K_b^{1/3} - 1}{1/3}, \quad (6)$$

or

$$K_{mix}^{1/3} = x_a K_a^{1/3} + x_b K_b^{1/3}. \quad (7)$$

*$K_\perp K_{II} = K_a K_b (x_a K_a + x_b K_b)/(x_a K_b + x_b K_a)$

$$= \left(\begin{matrix} x_a & x_b \\ K_a & K_b \end{matrix}\right)^2 \left(\begin{matrix} x_b & x_a \\ K_a & K_b \end{matrix} \middle/ \begin{matrix} x_a & x_b \\ K_a & K_b \end{matrix}\right)$$

$$\times \frac{x_a K_a + x_b K_b}{x_a K_b + x_b K_a}$$

$$= \left(\begin{matrix} x_a & x_b \\ K_a & K_b \end{matrix}\right)^2 \left\{ \left(x_a \left(\frac{K_a}{K_b}\right)^{x_b} + x_b \left(\frac{K_b}{K_a}\right)^{x_a}\right) \middle/ \left(x_a \left(\frac{K_b}{K_a}\right)^{x_b} + x_b \left(\frac{K_a}{K_b}\right)^{x_a}\right) \right\} \quad (4)$$

and the factor in curly brackets is exactly equal to 1 for $x_a = 0$, $\frac{1}{2}$, and 1, and is very close to unity for intermediate values of x_a.

It is however to be noted that the values of ε corresponding to the three principal directions for the individual slabs of Fig. 2 deviate from this mean figure of 1/3 by $+2/3$, $+2/3$ and $-4/3$, respectively, giving a standard deviation of $2/3$ for the mean. So that, inspite of the plausibility of ε being equal to 1/3 on the basis of the above argument with a three-dimensional array, it merely proves that, for an *isotropic mixture*,

$$\varepsilon = 1/3 \pm \alpha, \text{ where } \alpha << 2/3.$$

3. More Rigorous Proof of Formula

(i) *First Approximation*

The above limits for ε are very wide, and equation(7) therefore needs to be substantiated by more rigorous proof. We accordingly consider the arrangement of Fig. 3, which provides a closer approximation to an isotropic intimate mixture of the two substances, A and B. Fig. 3 comprises two composite slabs of the types shown in Figs. 2(a) and 2(b) respectively, arranged (at right angles) one above the other. Taking the y-axis and z-axis in the plane of the paper (Fig. 3) and the x-axis perpendicular to this plane, we easily find by a further application of the formulae 2 that*

$$K_x = K_{||} = x_a K_a + x_b K_b, \tag{8a}$$

$$K_y = \frac{1}{2}(K_\perp + K_{||})$$

$$= \frac{1}{2}\left\{\frac{K_a K_b}{x_a K_b + x_b K_a} + x_a K_a + x_b K_b\right\} \tag{8b}$$

$$1/K_z = \frac{1}{2}\left(\frac{1}{K_\perp} + \frac{1}{K_{||}}\right)$$

$$= \frac{1}{2}\left\{\frac{x_a}{K_a} + \frac{x_b}{K_b} + \frac{1}{x_a K_a + x_b K_b}\right\} \tag{8c}$$

K_y and K_z are readily shown to be very near to $K_a^{x_a} K_b^{x_b}$ in value. Thus

$$1/K_z = \frac{1}{2}\left(\frac{x_a K_b + x_b K_a}{K_a^{x_b} K_b^{x_a}} + \frac{K_a^{x_a} K_b^{x_b}}{x_a K_a + x_b K_b}\right)$$

$$\Big/ K_a^{x_a} K_b^{x_b} = (1+\delta)/\left(K_a^{x_a} K_b^{x_b}\right), \tag{8d}$$

where δ is zero for $x_a = 0, 1$, and has its maximum value for $x_a = x_b = 1/2$, when it is equal to

*It is of course to be understood that these formulae will apply strictly only if the temperature across the dividing planes, $A_1 B_1$, $A_2 B_2$, etc. in Fig. 3 is perfectly uniform.

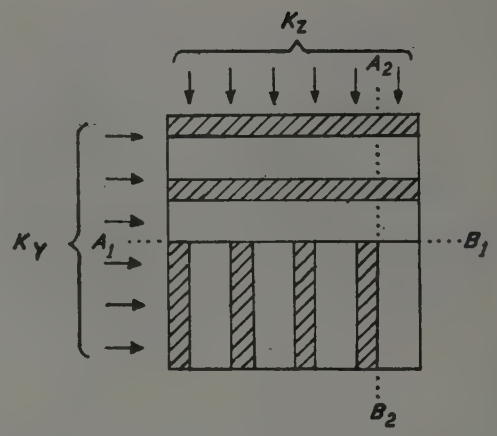

Fig. 3.—Composite block made up of two slabs of the type shown in Fig. 2 oriented so as to make the block more nearly isotropic.

$$\left\{\frac{1}{2}\left(\frac{K_a+K_b}{2\sqrt{K_a K_b}} + \frac{2\sqrt{K_a K_b}}{K_a + K_b}\right) - 1\right\}$$

$$= \frac{1}{2}\left(\frac{K_a + K_b}{2} - \sqrt{K_a K_b}\right)^2 \Big/ \left(\frac{K_a+K_b}{2}\sqrt{K_a K_b}\right),$$

which is only 0.13 for $K_a/K_b = 9$. Similarly

$$K_y = \frac{1}{2}\left(\frac{x_a K_a + x_b K_b}{K_a^{x_a} K_b^{x_b}} + \frac{K_a^{x_b} K_b^{x_a}}{x_a K_b + x_b K_a}\right) \times K_a^{x_a} K_b^{x_b}$$

$$= (1 + \delta') K_a^{x_a} K_b^{x_b}, \tag{8e}$$

where δ' is zero for $x_a = 0, 1$, and is a maximum for $x_a = x_b = 1/2$, this maximum value being the same as for δ. Thus, the mean of K_y and K_z will be equal to $(K_a^{x_a} \times K_b^{x_b})$ to a very high degree of accuracy, so that we may conclude (cf. equation(5)) that the formula for mean thermal conductivity, $K_{y,z}$, in these two principal directions corresponds to formula (3) with $\varepsilon = 0$. K_x, on the other hand, corresponds to $\varepsilon = +1$, cf. equations 8(a) and (3). If we take a random 3-dimensional stacking of the blocks of Fig. 3, the resultant K is again given by the mean of $K_{y,z}$ and K_x, weighted in the ratio of 2 to 1, and we can estimate that the value of ε in the formula for the isotropic mixture should be very close to $(2\times 0 + 1 \times (+1))/3 = 1/3$. The S.D. of this mean being now only 1/3 for an individual block, we have proved that for the three-dimensional stacking of the blocks, $\varepsilon = 1/3 \pm \alpha$, where $\alpha << 1/3$.

(ii) Second Approximation

The above analysis is an improvement on that given in section 2, insofar as the composite block is more nearly isotropic, and therefore the values of ε for the three principal directions vary less than before. A further improvement is effected by considering a block of the type shown in the inset to Fig. 4, which consists of slabs arranged together in three different orientations so as to give almost the same thermal conductivity in each of the three principal directions. It is seen that in each of these directions, the heat flow is parallel to the constituent layers in two of the slabs, and is perpendicular to these layers in the third. Therefore we have

$$K_{x,y} = K_x = K_y = 2/3\, K_{\parallel} + 1/3\, K_{\perp}$$
$$= 2/3\,(K_a x_a + K_b x_b) + 1/3\, \frac{K_a K_b}{x_a K_b + x_b K_a}, \qquad (9a)$$

and

$$1/K_z = \frac{2/3}{x_a K_a + x_b K_b} + \frac{x_a K_b + x_b K_a}{3\, K_a K_b} \qquad (9b)$$

If we denote the value of K calculated from equation (7) by K_{ideal}, then

$$K_{x,y} - K_{ideal}$$
$$= \frac{2\,K_a K_b (x_a^2 + \tfrac{1}{2} + x_b^2) + 2x_a x_b (K_a^2 + K_b^2)}{3(x_a K_b + x_b K_a)} - (x_a K_a^{1/3} + x_b K_b^{1/3})^3$$
$$= \frac{3K_a K_b + 2x_a x_b (K_a - K_b)^2}{3(x_a K_b + x_b K_a)} - (x_a^3 K_a + x_b^3 K_b + 3x_a x_b K_a^{1/3} K_b^{1/3} \times (x_a K_a^{1/3} + x_b K_b^{1/3}))$$
$$= \left\{ \frac{K_a K_b}{x_a K_b + x_b K_a} - (x_a^3 K_a + x_b^3 K_b) \right\} + x_a x_b \left\{ \frac{2}{3} \frac{(K_a - K_b)^2}{x_a K_b + x_b K_a} - 3K_a^{1/3} K_b^{1/3} (x_a K_a^{1/3} + x_b K_b^{1/3}) \right\}$$

Simple substitution shows that this difference is zero for $x_a = 0$ and for $x_a = 1$.
For $x_a = x_b = \frac{1}{2}$, it is equal to

$$\left\{ \frac{2K_a K_b}{K_b + K_a} - \frac{K_a + K_b}{8} \right\} + \frac{1}{4} \left\{ \frac{4}{3} \frac{(K_a - K_b)^2}{K_a + K_b} - \frac{3}{2} K_a^{1/3} K_b^{1/3} (K_a^{1/3} + K_b^{1/3}) \right\}$$
$$= \frac{1}{4} \left\{ \frac{3}{2} (K_a + K_b) - \frac{3}{2} K_a^{1/3} K_b^{1/3} (K_a^{1/3} + K_b^{1/3}) \right\} + \left\{ \frac{2K_a K_b}{K_a + K_b} - \frac{K_a + K_b}{2} + \frac{1}{3} \frac{(K_a - K_b)^2}{K_a + K_b} \right\}$$
$$= \frac{3}{8} \left\{ K_a - K_a^{2/3} K_b^{1/3} + K_b - K_a^{1/3} K_b^{2/3} \right\} + \left(\frac{1}{3} - \frac{1}{2} \right) \frac{(K_a - K_b)^2}{K_a + K_b}$$
$$= \frac{3}{8} (K_a^{1/3} - K_b^{1/3})(K_a^{2/3} - K_b^{2/3}) - \frac{1}{6} \frac{(K_a - K_b)^2}{K_a + K_b}$$
$$= \frac{3}{4} \frac{(K_a^{1/3} - K_b^{1/3})^2}{(K_a + K_b)/2} \left\{ \frac{K_a^{1/3} + K_b^{1/3}}{2} \times \frac{K_a + K_b}{2} - \left(\frac{K_a^{2/3} + K_a^{1/3} K_b^{1/3} + K_b^{2/3}}{3} \right)^2 \right\}.$$

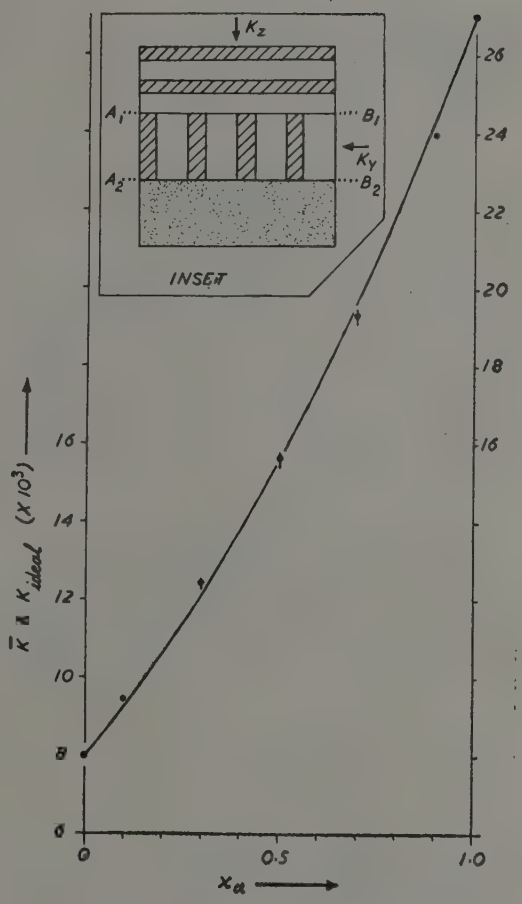

Fig. 4.—Graph showing the ideal variation of thermal conductivity for a mixture governed by the $K^{1/3}$ law proposed in this paper and the values calculated for the approximately isotropic block shown in the inset (made up of three slabs of the type sketched in Fig. 2). The dotted area indicates that the composite layers making up the slab are parallel to the plane of the paper.

From this we find

$$\left\{\frac{K_{x,y}-K_{ideal}}{K_{ideal}}\right\}_{x_a=\frac{1}{2}} \simeq \frac{3}{4}\,\frac{(K_a^{1/3}-K_b^{1/3})^2}{K_a+K_b} \times \frac{7}{3}\,\frac{(K_a^{1/3}-K_b^{1/3})^2}{K_a^{1/3}+K_b^{1/3}}, \quad (10a)$$

which can be shown to correspond to a value of ε given by the simplified formula,

$$(\varepsilon)_{x,y} = 1/3 + 7/8(K_a^{2/3}-K_b^{2/3})^2 / (K_a^{2/3}+K_a^{1/3}K_b^{1/3}+K_b^{2/3})^2. \quad (10b)$$

The term added to 1/3 is small, being nearly $0.1 \times \{(K_a^{2/3}-K_b^{2/3})/\overline{K^{2/3}}\}^2$, e.g. for a value of K_a/K_b as high as 4, the additional term is 0.08, giving $(\varepsilon)_{x,y}=1/3+0.08$. Similarly, the evaluation of $(K_{ideal}-K_z)$ gives

$$\left\{\frac{K_{ideal}-K_z}{K_{ideal}}\right\}_{x_a=\frac{1}{2}} \simeq \frac{(K_a-K_b)^2}{12K_aK_b} - 3\left(\frac{K_a^{1/3}-K_b^{1/3}}{K_a^{1/3}+K_b^{1/3}}\right)^2$$

$$\simeq \frac{11}{8}\,\frac{(K_a^{1/3}-K_b^{1/3})^2}{K_a^{1/3}K_b^{1/3}} \times \frac{(K_a^{1/3}-K_b^{1/3})^2}{(K_a^{1/3}+K_b^{1/3})^2}, \quad (10c)$$

which leads to the value of $(\varepsilon)_z$ corresponding to $K_a/K_b=4$ as $1/3-0.14$. From these two values of ε, we can deduce that the value for a three-dimensional stack of the nearly isotropic composite blocks of Fig. 4 will be given by

$$\bar{\varepsilon} = 2/3 \times (1/3+0.08) + 1/3 \times (1/3-0.14) = 0.34_0. \quad (11)$$

(iii) *A Numerical Example*

It is however still necessary to investigate the variation of $\overline{K}$, the weighted mean value of K, for values of x_a between 0 and 1/2 and also between 1/2 and 1.

This is best done by means of a numerical example. Taking $K_a=27\times10^{-3}$ and $K_b=8\times10^{-3}$, so that $K_a/K_b=3.4$, $K_a^{1/3}=0.3$ and $K_b^{1/3}=0.2$ we get the values given in Table 1 for K_{ideal}, $K_{x,y}$, and K_z for different values of x_a and x_b. It is seen that $K_{x,y}$ and K_z agree within about 2% over the whole range of compositions, thus showing that the composite block of Fig. 4 (inset) approximates very well to an isotropic mixture. The sixth column gives the values of $\overline{K}$, the weighted mean of $K_{x,y}$ and K_z. These values of $\overline{K}$ are plotted in Fig. 4 as solid circles, while the short vertical lines indicate the deviations of $K_{x,y}$ and K_z from $\overline{K}$. The variation of K_{ideal} is shown by the smooth curve, from which it is apparent that (a) $\overline{K}$ is exactly equal to K_{ideal} for $x_a=0$ and 1, and also for $x_a=0.51$, (b) $\overline{K}$ deviates from K_{ideal} by at most 2%, the deviations being distributed evenly about the curve, and (c) the best value of the index ε for overall agreement with $\overline{K}$ is the one used for K_{ideal}, i.e. 1/3.

The small discrepancies still remaining between $\overline{K}$ and K_{ideal} can be attributed to the fact that (a) oblique flow of heat has not been considered in the above analysis, and (b) the temperature over any one of the dividing planes such as A_1B_1, A_2B_2 in Fig. 4 is not strictly constant. Because the small discrepancies between $\overline{K}$ and K_{ideal} are evenly distributed about the curve for K_{ideal}, it can be anticipated that they will vanish when the defects in the analysis are removed.

4. Experimental Verification with Cellular Concretes

An excellent experimental test for the correctness of the formula derived above is in its application to the thermal conductivities of cellular materials such as cellular concrete, cork, etc., which can be considered to be isotropic mixtures of the entrapped air with the cement, wood, or other material involved. Since the conductivity of cement is of the order of 1.5×10^{-3} calories $cm.^{-1}\,sec^{-1}/°C.$, while that of air is 0.06×10^{-3}, the conductivities of cellular concretes will cover

TABLE 1.—COMPARISON OF K_{ideal} WITH $K_{x,y}$, K_z AND $\overline{K}$ FOR $\overline{K_a}=27\times10^{-3}$ AND $K_b=8\times10^{-3}$.

x_a	x_b	$K_{ideal}\times10^3$	$K_{x,y}\times10^3$	$K_z\times10^3$	$\overline{K}\times10^3$	$\frac{\overline{K}-K_{ideal}}{K_{ideal}}$	
0.0	1.0	8.00	8.00	8.00	8.00	0.0%	
0.1	0.9	9.26	9.47	9.43	9.46	+2.1%	
0.3	0.7	12.17	12.51	12.27	12.43	+2.1%	Root mean square value $= \pm 1.3\%$
0.5	0.5	15.63	15.78	15.36	15.64	+0.1%	
0.7	0.3	19.68	19.45	19.07	19.32	−1.8%	
0.9	0.1	24.40	24.00	23.90	23.97	−1.8%	
1.0	0.0	27.00	27.00	27.00	27.00	0.0%	

a decade of values from 1×10^{-3} to 0.1×10^{-3} cal. cm.$^{-1}$ sec.$^{-1}$/°C., and so a precise estimate can be made of the best value of the index ε that fits the experimental data. For a two-component system such as air and cement, the density ρ is given by $\rho = x_{air}\ \rho_{air} + x_{cement}\ \rho_{cement} \fallingdotseq x_{cement}\ \rho_{cement}$ (where x = parts by volume), to a sufficient accuracy because $\rho_{air} = 0.001$ g./ml. while $\rho_{cement} \sim 2$ g./ml. Thus we may take the density ρ of the cellular concrete as varying linearly with the porportion of cement by volume. Table 2 below gives the standard measured values of ρ and K for several cellular cements as given in the report of the Division of Building Research of the C.S.I.R.O. Australia[3] (1954), the standard deviation of the values of K being about 4%. In Fig. 5(a), K and also its logarithm are plotted against the density ρ, and it is seen that both graphs show a strong curvature, but in opposite directions. Since $\ln K = \lim_{n \to 0} (K^n - 1)/n$, the function ln K clearly corresponds to the value 'o' of the index ε. It follows that the correct value of the index ε lies between 1 (K–plot linear) and 0 (lnK plot linear). In order to determine the precise value of ε, it is useful to calculate the function $\varphi_\varepsilon(K) = ((K \times 10^4)^\varepsilon - 1)/\varepsilon$ for two values of ε, viz. 0.30 and 0.35, lying on either side of the expected value 1/3. (This function has the special feature that its value for $K \sim 1 \times 10^{-4}$ is practically independent of ε.) The corresponding points are plotted in Fig. 5(b), and are seen to lie fairly well on the straight lines joining the extreme points drawn therein. However, a close inspection of the deviations of the experimental points from the straight lines shows that they are preponderantly positive in the plot for ε=0.30 and somewhat negative in the case of ε=0.35. Therefore the best experimental value of ε may be taken as 0.33 ± 0.02, which is in excellent agreement with the theoretical value of 1/3 derived in equations (6) and (7) and proved more rigorously in section 3. This firmly establishes the $K^{1/3}$ law

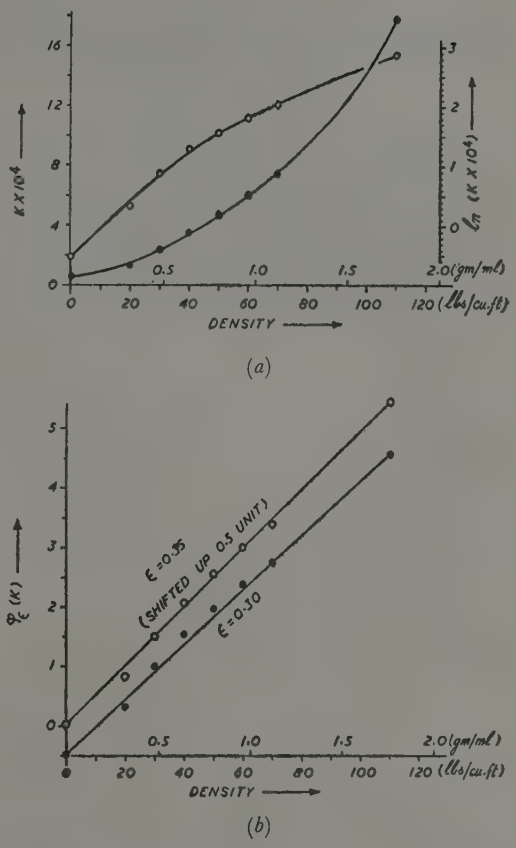

Fig. 5.—Comparison of experimental data on cellular concretes with the theoretically deduced $K^{1/3}$ law:

(a) graphs of K_{expt} and ln (K_{expt}) against density for cellular concretes: K_{expt} solid circles; ln (K_{expt}), hollow circles.

(b) graphs of $\varphi_\varepsilon(K) = ((K \times 10^4)^\varepsilon - 1)/\varepsilon$ for two values of ε, showing that the best value of ε lies in between them.

TABLE 2.—MEASURED CONSTANTS FOR CELLULAR CONCRETE (AT 75 °F.) SHOWING THE APPLICABILITY OF THE $K^{1/3}$ LAW.

Density, ρ (lbs./cu. ft.)	0.05 (Air)	20	30	40	50	60	70	110 (breeze concrete)
K {British units		0.4	0.7	1.04	1.38	1.77	2.17	5.2
K {cal. cm.$^{-1}$ sec.$^{-1}$/°C. $\times 10^4$ ..	0.6_0	1.3_8	2.4_1	3.5_8	4.7_5	6.0_9	7.4_7	17.9
ln (K × 10⁴) ..	-0.5_{10}	$+0.3_{22}$	$+0.8_{80}$	1.2_{75}	1.5_{59}	1.8_{05}	2.0_{10}	2.8_{85}
$((K \times 10^4)^{0.3} - 1)/0.3$	-0.4_{73}	$+0.3_{39}$	$+1.0_{07}$	1.5_{53}	1.9_{86}	2.3_{96}	2.7_{59}	4.5_{87}
$((K \times 10^4)^{0.35} - 1)/0.35$	-0.4_{68}	$+0.3_{40}$	$+1.0_{30}$	1.6_{08}	2.0_{72}	2.5_{18}	2.9_{18}	4.9_{85}

for thermal conductivity of a mixture of x_a parts (by volume) of a component of conductivity K_a with x_b parts of a component of conductivity K_b, viz.

$$K_{\text{mixture}}^{1/3} = x_a K_a^{1/3} + x_b K_b^{1/3}. \qquad (7)$$

5. Some Applications to Other Materials

It is interesting to use equation (7) to calculate the thermal conductivities of cork and rice husk ash, and to compare these values with those determined by experiment. For cork of density 0.16 g./ml., the proportion by volume of air is given by

$$x_{\text{air}} = 1 - \left(\frac{0.16}{\rho_{\text{wood}}}\right) = 1 - \frac{0.16}{0.8} = 0.8$$

Taking the mean thermal conductivity of ordinary wood as 0.5×10^{-3} cal. cm.$^{-1}$ sec.$^{-1}$/°C., from the tables, we get

$$K_{\text{cork}}^{1/3} = 0.8\, K_{\text{air}}^{1/3} + 0.2\, K_{\text{wood}}^{1/3},$$

$$\text{i.e. } K_{\text{cork}} = \{0.8 \times (0.06 \times 10^{-3})^{1/3} + 0.2 \times (0.5 \times 10^{-3})^{1/3}\}^3 \text{ cal. cm.}^{-1} \text{ sec.}^{-1}/°\text{C.}$$

$$= (0.314 + 0.159)^3 \times 10^{-3} = 0.10_5 \times 10^{-3} \text{ cal. cm.}^{-1} \text{ sec.}^{-1}/°\text{C.}$$

which is in excellent agreement with the tabulated value of 0.11×10^{-3}.

Rice husk ash is essentially a lattice work of SiO_2 with air in the spaces, as appears in the photograph of Fig. 6(a). X-ray powder photographs of the ash (Fig. 6(b)) indicate that the SiO_2 is mostly in the form of cristobalite, which has a density of 2.4 g./ml. and a thermal conductivity of 18×10^{-3} cal.$^{-1}$ cm. sec.$^{-1}$/°C. However, there is a strong possibility of a certain amount of amorphous silica ($K = 4 \times 10^{-3}$ cal. cm.$^{-1}$ sec.$^{-1}$/°C.), being present, and assuming a ratio of 2:1 for these two constituents, we can estimate the effective K for the SiO_2 of the ash as $(12 \pm 4) \times 10^{-3}$ cal. cm.$^{-1}$ sec./°C. From the measured density, 0.2 g./ml., of the ash (Table 1 in Part I)[1] we get

Fig. 6(a).—Photomicrograph of a particle of rice-husk ash (approximately × 100) showing its cellular structure.

$x_{SiO_2} = 0.2/2.4 = 0.08_3$, and $x_{\text{air}} = 1 - 0.08_3 = 0.91_7$

Therefore $K_{\text{ash}} = \{0.917 \times (0.06 \times 10^{-3})^{\frac{1}{3}} + 0.083 \times ((12 \pm 4) \times 10^{-3})^{\frac{1}{3}}\}^3$

$= (0.360 + 0.186 \pm 0.022)^3$

$= (0.16_4 \pm 0.01_9) \times 10^{-3}$ cal.cm.$^{-1}$sec.$^{-1}$/°C.,

which compares well with our measured value[1] of 0.15 ± 0.02. It is noteworthy that a cellular concrete of the same density as the ash would have a K value of 0.11×10^{-3} as given by the graphs of Fig. 5.

The good agreement with experiment seen in these two examples affords additional support for the correctness of formula (7), which can be recast into a more useful form for this type of application, viz.

$$K_{\text{calc}} = \left\{ K_{\text{air}}^{1/3} \left(x_{\text{air}} + x_b \left(\frac{K_b}{K_{\text{air}}}\right)^{\frac{1}{3}}\right)\right\}^3$$

$$= K_{\text{air}}\{1 - x_b + x_b (K_b/K_{\text{air}})^{\frac{1}{3}}\}^3$$

$$= K_{\text{air}}\{1 + (1-P)((K_b/K_{\text{air}})^{1/3} - 1)\}^3 \qquad (12)$$

with P, the porosity of the material, being given by $(\rho_b - \rho)/(\rho_b - \rho_{\text{air}}) \simeq 1 - \rho/\rho_b$, where ρ is the density of the composite material, and ρ_b that

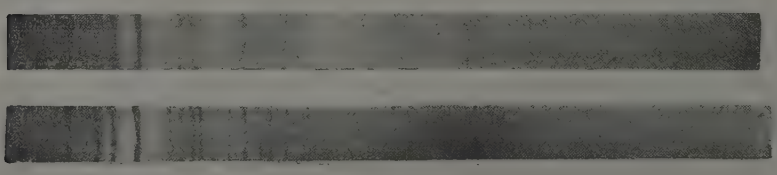

Fig. 6 (b).—X-ray powder pattern of the ash compared with a standard pattern of cristobalite (both taken with filtered CuK radiation).

of the component B. It is to be noted here that the experimental results cited above extend only upto a porosity of about 0.9. Further examination of the case of materials with higher porosities is in hand, and will be reported separately.

Acknowledgements

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SOME VALUABLE CONSTITUENTS OF OIL CAKES FROM EAST PAKISTAN

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Oil cakes are usually treated as waste products in East Pakistan. Their intrinsic values have never been considered; they are either used as cattle feed or as fertilizer. If proper statistics of the production of oil cakes are made, the estimated loss will run very high. Our attention was drawn to this problem when a local mill owner quoted the quantity of production of cakes in his one firm running upto lacs of maunds per annum.

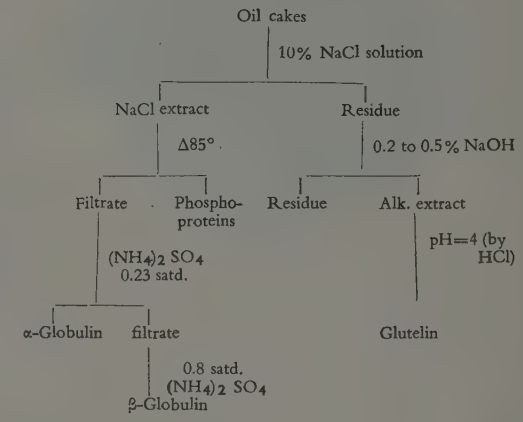
Two types of oil cakes are available in East Pakistan : (a) machine-pressed and (b) 'ghani'-pressed cakes. Most city mills tend to extract all oils from cakes by mechanical means and hence the food values of their cakes have been found to be small. The ghani-pressed cakes are available both from the cities as well as from the country sides. They do not deteriorate much in colour and quality. Their food values are also significant, as it has been found in this paper. Moreover, they contain more oil and good flavour. As far as the mustard cakes are concerned, the ghani-pressed varieties have been found to contain larger quantities of allyl isothiocyanate (mustard odour principle) and other valuable nutrients. From these points of view, the ghani-pressed cakes of mustard, sesame and coconut have been analyzed for various constituents. The survey of literature indicated lack of such analyses for the East Pakistan types of these cakes.

Experimental

Materials.—The seeds of mustard and sesame, as well as ripe coconuts were purchased from the local markets. The seeds and coconut kernel were thoroughly dried and oils in each case were pressed out by ghani, well cleaned ahead. The cakes were dried again and powdered for experiments.

Procedures.—The cakes were initially freed from residual fats by solvent extraction. The defatted cakes were used for different analyses of ash,[1] protein,[2] fibre,[3] starch,[4] free reducing sugar,[5] vitamin E[6] and A,[7] and finally, fractionation of proteins through salt solubilization method.[8] The solubilization method is briefly represented in the chart.

Chart



The percentage purity of each fraction was determined by protein contents.[2] The minerals, such as, calcium, magnesium, potassium, sodium, iron and phosphorus, were also determined by the standard procedures.[9] The last two minerals have also been determined colorimetrically.[10] The three cakes have been subjected to steam distillation.[11] The processes of leaching with water was carried out by shaking the cakes with water. The water extract on boiling was allowed to precipitate out protein constituents and the filtrate was evaporated to dryness for other water-soluble materials.

The fat, non-saponifiable matter,[12] saponification value,[13] free fatty acid,[13] iodine value,[13] sterols[14] and phospholipids,[15] were determined according to the standard methods. The fat-soluble vitamins[15] (E and A) were also estimated in the fats.

Results and Discussion

The ghani-pressed cakes retain the original flavour, but the machine-pressed ones become somewhat darkened in colour and different in odour. Hence, the nutrients, like minerals (ash), protein, fat, carbohydrates and vitamins (Table 1), may be obtained in better conditions in ghani-pressed cakes. The high percentage of protein in mustard cake has increased its value greatly. Though this cake is not edible, its proteins can be used for various other purposes: glue, plastic and paints. The water extract of mustard cake

contains saponins with some cleansing properties. Each cake has some water-soluble proteins that coagulate on heating as shown in Table 1. The steam distillation did not yield any product, except some traces of odorous principles. Vitamin E in mustard cake is an added asset.

TABLE 1.—NUTRITIVE VALUE OF MUSTARD, SESAME AND COCONUT CAKES.
(g. per 100 g. of the substances).

Analysis	Mustard cake	Sesame cake	Coconut cake
Moisture ..	12.0	7.3	10.3
Ash ..	10.3	11.6	7.1
Total protein ..	40.1	34.1	15.3
Fat ..	13.4	12.6	23.6
Fibre ..	8.9	20.6	13.0
Starch (acid hydrolysis)	14.6	10.2	28.5
Free reducing sugar	1.2	1.0	1.1
Vitamin E ..	Considerable	Traces	nil
Vitamin A ..	nil	nil	nil
Odour ..	Pungent	Strong sesame-like	Appetizing
Colour ..	Greyish yellow	Greyish black	Almost white
Water-leached protein constituents	10.02	3.45	3.67
Water-soluble .. (Sugar, inorg. etc.)	12.6	25.5	23.59

The solubilization of proteins through salts has been shown in Table 2. This suggests the importance of the proteins present in cakes. The phosphoproteins and globulin fractions in cakes may have far-reaching biological values. It may be noted that they can be isolated in pure conditions through proper methods of reprecipitation and dialysis.[8] These specific proteins may be used as food additives or in pharmacological preparations.

TABLE 3.—CHARACTERISTICS OF RESIDUAL FATS IN CAKES.

Analysis	Fats from		
	Mustard cake	Sesame cake	Coconut cake
Total fats ..	13.40	12.60	23.60
Non-saponifiable matter ..	4.80	5.10	2.20
Saponification value ..	173.60	186.80	248.60
Free fatty acids ..	0.76	1.26	0.23
Iodine value ..	97.0	106.0	14.0
Sterols ..	1.35	2.60	1.18
Phospholipids ..	nil	nil	nil
Odour ..	Pungent	Tolerable sesame-like	Nice coconut-like
Odour tolerance (acceptability as food)	+ + +	+ +	+ + +
Colour ..	Deep yellow	Light yellow	Almost colourless
Vitamin E ..	Considerable	Traces	nil
Vitamin A ..	nil	nil	nil

TABLE 2.—PERCENTAGE OF DIFFERENT FRACTIONS OF PROTEIN ISOLATED FROM DIFFERENT CAKES BY SALT SOLUBILIZATION METHOD.

Protein fractions	Mustard cake		Sesame cake		Coconut cake	
	Protein fractions %	Purity of protein fractions %	Protein fractions %	Purity of protein fractions %	Protein fractions %	Purity of protein fractions %
α-Globulin	4.20	88.55	5.40	93.25	0.59	—
β-Globulin	3.24	87.15	3.60	97.31	0.51	—
Glutelin	6.10	81.72	8.76	68.44	2.51	—
Phosphoprotein	12.30	60.72	20.00	65.94	2.10	—

Table 4.—Inorganic Elements in Different Cakes.

Elements	Amount present in 100 g. of ash formed from			Amount present per 100 g. of air dried oil cake		
	Mustard oil cake	Sesame oil cake	Coconut oil cake	Mustard	Sesame	Coconut
Calcium	9.213	10.112	4.579	0.767	0.871	0.2322
Magnesium	6.275	5.055	4.600	0.521	0.587	0.2326
Potassium	10.940	6.271	27.750	0.914	0.728	1.407
Sodium	0.306	0.490	2.441	0.022	0.057	0.124
Iron	0.038	2.920	0.267	0.0031	0.251	0.003
Phosphorus	6.650	9.266	7.604	0.554	1.076	0.385
K (as oxide)	16.500	7.545	33.500	1.372	0.876	1.699

Table 3 indicates the nature of fats extracted from the respective cakes. They are found to be of similar properties as the main bulk of oil initially processed. The larger quantities of the non-saponifiables may be removed by refining processes.[16] It is surprising that the cakes do not contain any phospholipids which usually accompany cakes. It may be attributed to the climatic or soil conditions of the land.

Table 4 gives the mineral contents of each cake. For the advantage of various workers, the minerals have been calculated on the basis of both ash and original oil cake (dried). Calcium in mustard and sesame cakes deserves particular attention. (Potassium (coconut in particular) and sodium are interesting to coronary patients.) Iron and phosphorus in sesame cake bid for better nutritive values. In general, the mineral contents in all cakes are very appreciable. Sesame cake has uniformly high levels of minerals estimated. From the point of view of odour, the sesame and coconut cakes may be turned into edible food products.

Acknowledgement

The authors wish to thank Dr. Salimuzzaman Siddiqui for his helpful suggestions during the progress of the work. They also express their greatful appreciation to Messrs A.K.M. Moslem Ali, S. Adhikari and H. C. Das for their assistance in the experimental work.

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DEVELOPMENT OF RAPID METHODS FOR THE ESTIMATION OF THE OIL CONTENT OF SINGLE COTTONSEEDS

Part I.—An Oil-Expression Technique

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The rapid estimation of the oil content of a single cottonseed is a matter of considerable importance to studies in cotton breeding relating to the developement of high oil content varieties. If a simple method for this estimation can be evolved, it should be possible quickly to examine a few seeds from an individual plant and use the rest for propagation in breeding experiments. Rapid chemical and electrical methods have been developed by some workers,[1,2,3] and they give good results with several grammes of finely crushed material, but no rapid micro-analytical technique appears to have been developed for work with a single cottonseed. A further elaboration of such a micro method would be to develop a non-destructive oil estimation technique, which does not impair the viability of the seed.

Three methods, each based on a different principle, have been studied in these laboratories: (1) expression of the oil (under pressure) into a set of filter papers followed by estimation of the area of the oil spot, (2) measurement of the density of the oil seed after dehulling, and (3) measurement of the electrical constants of the oil seed under several different conditions. The present paper deals with the first of these methods, which is destructive, while the second and third are both non-destructive, and do not affect the viability of the seed. The results of work on the latter two methods will be communicated in subsequent papers of this series.

Estimation of the Oil Content of Single Seeds by Expression Method

The oil seeds were crushed between several discs of filter paper in order to study the relation between the weight of the seed and the area of the resultant oil spot. The use of several discs of filter paper was adopted to reduce possible error through variable escape of the oil on to the plates of the press. In this study, dehulled seeds from a single variety (L.S.S.) of cotton plant were placed between six discs of Green's No. 401 filter paper, three on either side, and pressed between the plattens of a small 10 ton laboratory bench hydraulic press at various loads ranging from ½ ton to 10 tons. On removal from the press, a well defined nearly circular transluscent patch of oil was visible on the filter papers. The areas of these oil spots on the two innermost filter papers were determined by measuring two mutually perpendicular diameters for each, and the overall mean area was noted, the accuracy being of the order of ±5 sq. mm. in a spot area of 80 to 200 sq. mm. The procedure was repeated six times for each particular load, using six weighed kernels. The results obtained with several loads from 1/2 ton to 10 tons are given in the first four columns of Table 1, and are plotted against the weights of the respective kernels in Fig. 1. The points for each load lie fairly well along the straight line through the origin, the mean scatter about these lines being 5%, corresponding to nearly ±1% in oil content. Thus the areas of the oil spots are closely proportional to the weights of the kernels, from which it can be concluded that, for seeds of a single variety, the ratio of oil content to weight of kernel is nearly constant.

The slopes of the straight lines of Fig. 1, representing the sensitivity, i.e. mean area of the

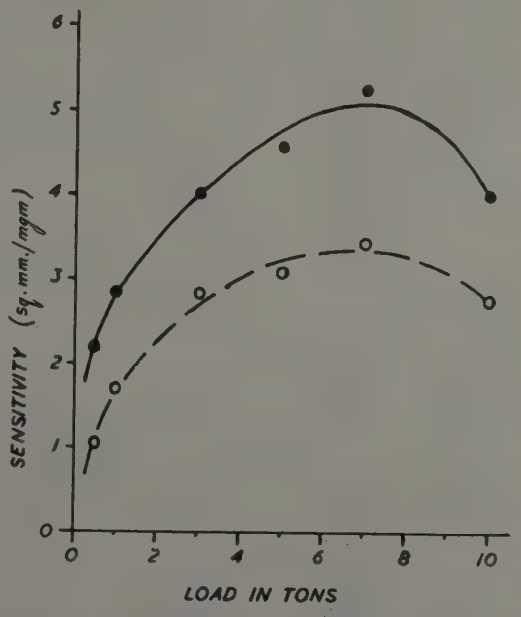

Fig. 2.—Sensitivity curves showing the sensitivity as area of spot per mg. of kernel against the crushing load. Full line for total area of spot, and broken line including correction for area of crushed kernel.

TABLE 1.—SINGLE SEEDS OF L.S.S. VARIETY OF COTTON : EXPRESSION OF OIL BETWEEN SIX FILTER PAPERS (GREEN'S 401).

Total load (tons)	Weight of cotton seed kernel in mg.	Mean total area of oil spot (sq. mm.)	Total area per unit mass (sq. mm./mg.)	Mean area of pressed seed in sq. mm.	Difference (area of spot-area of seed) sq. mm.	Difference per unit mass (sq. mm./mg.)
	46.0	200	4.3_5	70	130	2.8_2
	50.4	188	3.7_3	67	121	2.4_0
	55.3	206	3.7_2	63	143	2.58
10	33.8	154	4.5_5	44	110	3.2_5
	42.8	153	3.57	53	100	2.3_3
	37.9	165	4.3_5	49	116	3.06
			mean=4.04±0.21			mean=2.74±0.17
	45.2	251	5.57	88	163	3.59
	39.7	212	5.34	79	133	3.3_5
	44.8	232	5.1_7	86	146	3.2_5
7	47.2	254	5.38	71	183	3.8_7
	56.5	284	5.0_2	95	189	3.34
	56.7	284	5.00	104	180	3.1_7
			mean=5.25±0.11			mean=3.4_2±0.11
	44.8	200	4.46	67	133	2.96
	48.5	219	4.51	81	138	2.8_4
	37.9	188	4.96	59	129	3.4_0
5	48.7	214	4.39	70	144	2.9_5
	43.9	200	4.53	59	141	3.2_1
	51.0	232	4.54	70	162	3.1_7
			mean=4.56±0.07			mean=3.09±0.10
	36.0	143	3.97	50	93	2.59
	42.3	170	4.02	49	121	2.8_6
	35.8	164	4.58	47	117	3.26
3	39.4	148	3.7_5	47	101	2.56
	35.2	137	3.8_9	35	102	2.8_9
			mean=4.0_4±0.12			mean=2.8_3±0.11
	31.2	90	2.8_8	44	46	1.4_7
	35.9	104	2.8_9	44	60	1.6_7
	37.8	113	2.97	38	75	1.98
1	34.4	94	2.7_3	27	67	1.94
	31.6	86	2.7_2	44	42	1.3_2
	30.4	90	2.96	35	55	1.80
			mean=2.86±0.05			mean=1.7_0±0.12
	34.6	63	1.8_2	33	30	0.86
	39.4	86	2.18	36	50	1.26
	37.8	67	1.7_7	33	34	0.89
½	28.4	71	2.50	41	30	1.0_5
	38.2	104	2.7_2	60	44	1.1_5
	43.8	95	2.1_6	44	51	1.16
			mean=2.19±0.15			mean=1.06±0.07

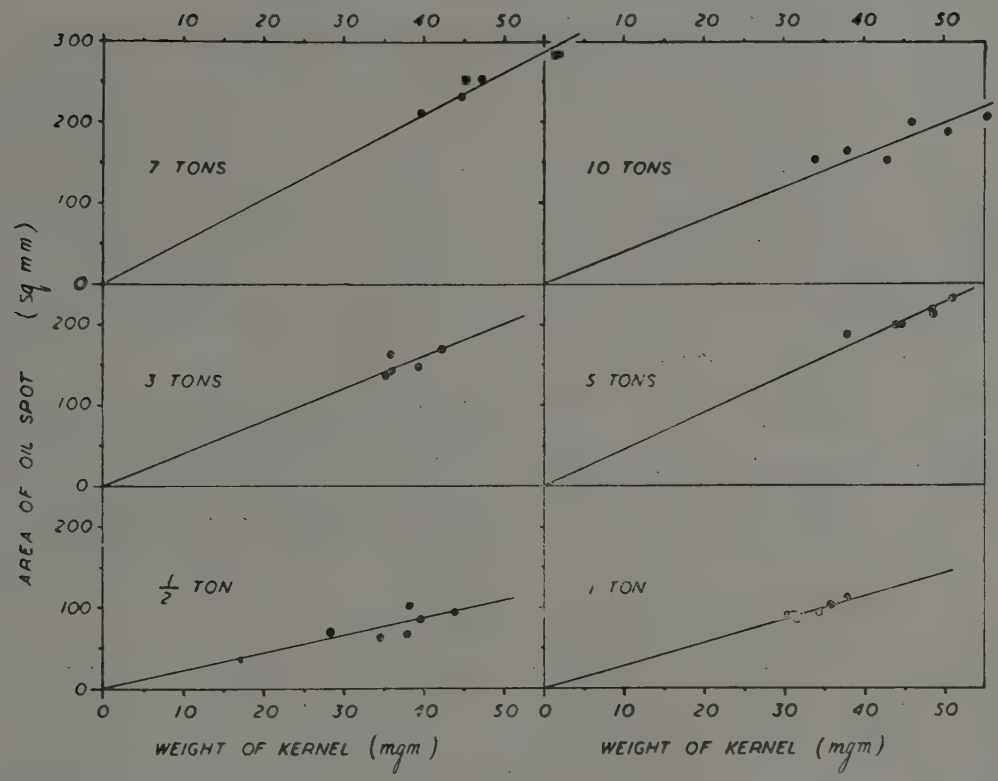

Fig. 1.—Set of graphs for the area of oil spot against weight of L.S.S. cottonseed kernels crushed between "Green's No. 401" filter papers at various loads from 1/2 ton to 10 tons.

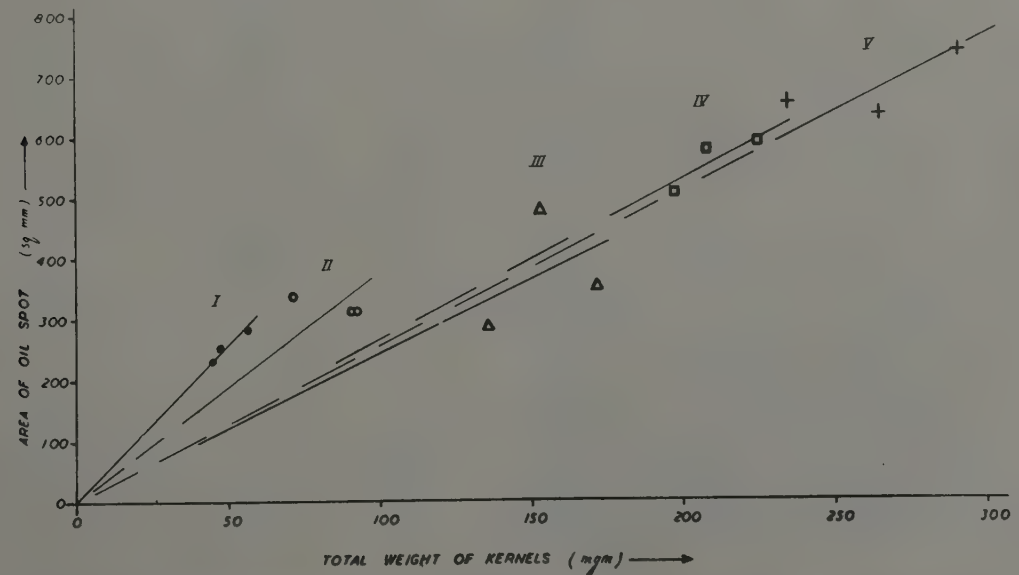

Fig. 3.—Set of graphs for simultaneous crushing of several closely placed seeds, showing area of the spot against total weight of kernels. Solid circles for single seeds; hollow circles for two seeds; triangles for three seeds; squares for four seeds; and crosses for five seeds.

spot per milligram of kernel, are plotted against load in Fig. 2. This sensitivity increases steadily with load upto 7 tons (solid circles and full line in Fig. 2), after which it drops somewhat, indicating that 7 tons is the optimum load in respect of sensitivity for this method of oil estimation. The foregoing data demonstrate the feasibility of this technique for obtaining an accuracy of 1% in the estimation of oil content, provided that loads approaching this optimum value are used. The last three columns of Table 1 show the change in the sensitivity produced by subtracting the area of the crushed kernel from total area of the oil spot, the corresponding sensitivity curve being drawn with a broken line in Fig. 2.

Experiments with Several Seeds Crushed Together

A further series of experiments was conducted to study the effect of crushing several seeds together between the filter papers. The load used was 7 tons, and each experiment was repeated three times. The results are given in Table 2, and the areas of the oil spots are plotted in Fig. 3 against the total weight of the kernels for 1,2,3,4 and 5 seeds. It will be seen from this figure that (a) the sensitivity decreases with increasing number of oil seeds, and (b) the scatter of the points about the lines through the origin is considerably greater for the experiments with multiple seeds than for the single seeds. The first effect is readily understood if we consider the total load of 7 tons to be equally distributed among the seeds being crushed, so that the present experiments actually correspond to loads of 7/2, 7/3, 7/4 and 7/5 tons, respectively, on the individual seeds. This explanation is confirmed by the comparison, shown in Table 3, between the slopes of the lines of Fig. 3 with the sensitivities corresponding to the above loads in Figs. 1 and 2. The steeper drop with increasing number of seeds observed in the experiments with multiple seeds is presumably due to obstruction of the flow of oil by the neighbouring kernels. The increased scatter of the points in Fig. 3 is more difficult to explain, and only a part of it can be attributed to statistical variations in the oil content of the seeds of different plants of the variety used in the present study.

TABLE 2.—SIMULTANEOUS CRUSHING OF SEVERAL SEEDS (FILTER PAPER: GREEN'S 401) SEEDS OF L.S.S. COTTON; TOTAL LOAD = 7 TONS.

No. of cotton-seed kernels	Weight in mg.	Mean total area in sq. mm.	Total area (sq. mm.) per mg. of kernel	Whole area of the pressed seeds in sq. mm.	Difference (area of spot-area of seeds) in sq. mm.	Difference (sq. mm.)per mg. of kernel
1	44.8	232	5.17	86	146	3.25
	47.2	254	5.38	71	183	3.87
	56.5	284	5.0_2	95	189	3.34
			mean $=5.1_9$			mean $=3.4_8$
2	92.2	314	3.40	188	126	1.36
	90.8	314	3.4_5	141	173	1.9_0
	71.3	338	4.74	122	216	3.0_2
			mean $=3.8_6$			mean $=2.0_7$
3	135.5	288	2.1_8	153	135	0.9_9
	171.5	354	2.06	132	222	1.2_9
	153.0	481	3.14	225	256	1.6_7
			mean $=2.4_6$			mean $=1.31$
4	208.0	582	2.7_9	270	312	1.50
	197.1	509	2.58	240	269	1.36
	224.8	593	2.6_3	306	287	1.27
			mean $=2.6_6$			mean $=1.37$
5	264.4	637	2.4_0	298	339	1.2_8
	290.8	741	2.5_5	312	429	1.47
	233.8	657	2.8_1	253	404	1.7_2
			mean $=2.5_8$			mean $=1.49$

TABLE 3.—COMPARISON OF ACTUAL AND EXPECTED SENSITIVITIES FOR MULTIPLE SEEDS.

No. of seeds	1	2	3	4	5
Load per seed (tons) ..	7	3·5	2·3	1.8	1·4
Actual sensitivity (sq. mm./mg.)	5·2±0.1	3·9±0·5	2.5±0.3	2·7±0.1	2.6±0.2
Smoothed „ „ „	5·2±0.1	3·7±0·3	2·9±0.3	2.6±0.2	2·4±0.2
Expected sensitivity (sq. mm./mg.) from Fig. 2	5·1	4·2	3.6	3·3	3·1

Comparison between Results of Extraction and Expression Methods of Estimation of the Oil Content

For this purpose, the measurements on single seeds were also carried out with seeds of another variety of cotton, namely M4, using three different loads near the optimum, viz., 5 tons, 7 tons, and 10 tons, so as to determine the ratio of the oil contents for the M4 and L.S.S. varieties. When the same filter paper and load are used for both varieties, the percentage of oil can be taken as proportional to the area of the oil spots per mg. of kernel. This area per mg. was determined for these three loads, and its ratio to the corresponding quantity for the previously examined variety (L.S.S.) of cottonseed is given in Table 4 for the three loads used. This ratio appears to depend to some extent on the crushing load, with a maximum value at about 7 tons, but the standard errors indicate that this dependance on load is not statistically significant. The overall mean value of the ratio is found in Table 4 to be 0.75±0.04, which is in satisfactory agreement with the ratio 0.71 calculated * from the recorded values[4] of oil content based on the extraction method of estimation on these two varieties as obtained in 1957-58.

TABLE 4.—RATIO OF PERCENTAGE OIL CONTENT FOR M/4 AND L.S.S. VARIETIES.

Crushing load	Ratio from total area of oil spot	Ratio from area of oil spot minus area of crushed kernel	Mean
10 tons	0.83_7	0.70_8	0.77±0 06
7 tons	0.81_6	0.80_7	0.81±0.00
5 tons	0.72_0	0.63_9	0.68±0.04
Mean	0.791±0.05	0.718±0.06	0.75±0.04

Discussion

The above comparison shows that the indications of oil content given by the expression method can be relied upon to about 1 part in 30, corresponding to nearly ½% oil content, which accuracy compares favourably with that of the extraction methods. The time taken for one determination is of the order of five to ten minutes, which is a great advantage over even the (recently developed) rapid extraction methods ,[1,2] which require from 2 to 8 hours for a single estimation and an average of half an hour per sample if 50 samples are run simultaneously. As against 0.1 g., which is the average weight of the whole seed, samples of 2 to 5 g. are required in the rapid extraction methods for a single estimation of the oil content. The microchemical method described by Iwanoff[5] uses seed fragments (weighing 5-20 mg.), but the oil extraction and estimation techniques are involved and again require several hours.

Two advantages peculiar to the oil expression technique are that (a) it provides a simple means of studying variations within a single variety and even among the seeds from a single plant, of which some indication is given by the scatter of the experimental points about the straight lines in Fig. 1, and (b) the oil spot provides a record of the measurement. This oil spot spreads slowly by diffusion (over a period of several days) at ordinary temperatures, but its boundary is initially very sharp, and it can be traced out with a pencil or developed by

*The agreement would probably be better when allowance is made for the difference between the relative weights of hull and kernel in the two varieties.

spraying with a suitable reagent. Further work is being directed towards refinement of the technique described in this paper and its comparison with the corresponding micro-chemical estimation of oil content of single seeds.

Acknowledgements

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Note Added in Proof:—For the expression method described above, a constant can be worked out connecting the % oil content (on whole seed basis) with the area of oil spot (in sq. mm./mg. of kernel). For Green's No. 401 filter paper and a crushing load of 7 tons, the foregoing data give a value of 3.6 ± 0.1 for this constant.

SPECTROPHOTOMETRIC STUDY OF MERCURIC CHLORIDE-DIPHENYLCARBAZONE COMPLEX BETWEEN 4000° and 7000°A

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Because the estimation of mercury in small amounts is important[1,2] in several chemical reactions, it was considered useful to study quantitatively the absorption spectrum of mercuric chloride complexes, using the simple spectrophotometric technique. Since the simple salt ($HgCl_2$) as such is transparent in the visible region of the spectrum, it was treated as usual with one of the reagents used to render it coloured, the departure being that disphenylcarbazone was used instead of diphenylcarbazide.[1]

Consider two solutions of a given substance of thicknesses t_1 and t_2, respectively, and concentrations C_1 and C_2, respectively. If light of the same intensity is incident on each and if intensities of transmitted beams are equal, i.e.

$I_{t_1} = I_{t_2}$, then from the Lambert-Beer law,

$$I_{t_1} = I_0\, 10^{-C_1 K t_1} = I_0\, 10^{-C_2 K t_2} = I_{t_2},$$

therefore $C_1 t_1 = C_2 t_2 = 1/K \log_{10} (I_0/I_t)$.

Hence if t_2 and either C_1, t_1 or K are known, C_2 may be determined. The extinction coefficient K depends on the wavelength and on the nature of the solution, and it can be obtained from the relation :

$$C = 1/K \log (I_0/I_1) = D/K$$

where $D = \log (I_0/I_1)$ is the optical density of 1 cm. thickness of the solution.

Experimental Details

A Hilger-Nutting polarizing photometer was used in conjunction with a constant deviation spectrometer. The light source used was a Pointolight 100 candle power lamp, kept in a housing, cooled by ventilators and cooling fins. The light from the source after being divided by the double system of glass rohmbs passes through two optically identical cells, one of which contains the test solution and the other the blank. Finally before entering the spectroscope (which allows light of the wavelength set on the drum to pass through the eyepieces) the two beams in juxtaposition pass through another Nicol, which can be rotated by a remote control so as simultaneously to increase the intensity of light in one beam and to reduce that in the other. The intensities of the two spectra are made equal by rotating the plate holding the Nicol prism, which acts as photometer, and the optical density for the particular wavelength set on the drum is then read directly from the scale. To map the whole spectrum in the visible region, this procedure was repeated generally at 10 millimicrons intervals with smaller 5 millimicrons intervals near the absorption maxima.

The solutions were prepared in ethyl alcohol, which was 99.9% pure, and were standardized by usual methods. The solutions were prepared in Pyrex B Class measuring flasks corrected for temperature, and it was observed that they remained quite stable for nearly two hours. In this appreciable period of stability, the whole absorption spectrum was scanned on the Hilger-Nutting spectrophotometer, special care being taken to avoid any impurity in the solution or specks of dirt sticking to the windows of absorption cell. All the vessels were placed in soap solution for nearly twelve hours, and then washed with chromic acid, distilled water, and finally several times with ethyl alcohol. Immediately before use, the cells were rinsed many times with the solutions to be placed in them.

Results and Discussion

The absorption curves of the test solution at various concentrations are drawn in Fig. 1, in which the optical density is taken along the ordinate and the abscissae represent the wavelengths in millimicrons. The molar extinction coefficients for λ_{max} have been calculated both with and without correction for background, and are indicated in Table 1.

From the curves and the table, one can conclude that the departure from Beer's law, when the

TABLE 1.—EXTINCTION COEFFICIENTS.

Concentration	M/500	M/750	M/1000	M/1250	M/1500	M/2000
Molar extinction coefficient at λ_{max} (570 ± 15mμ)/Without correction ..	348	339	309	284	302	260
With correction	225	240	235	250	260	250

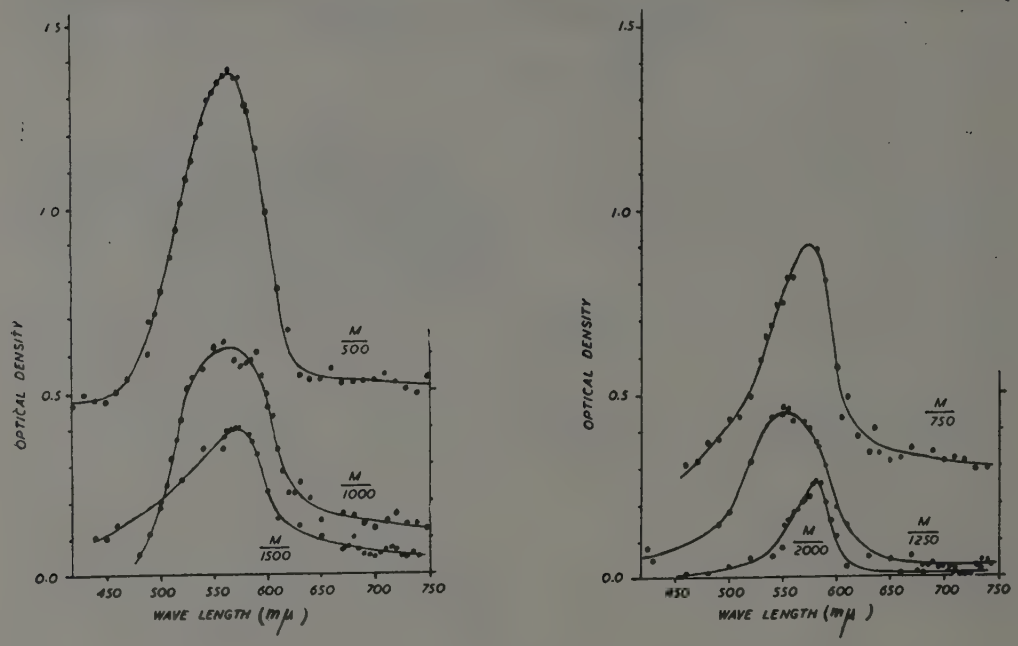

Fig. 1.—Absorption curves for different concentrations of mercuric chloride-diphenylcarbazone complex.

correction for background is made, is not very significant, and it can be seen that the optical density is proportional to the concentration to within ±5% upto as high a concentration as M/500. The absorption maxima at different concentrations lie pretty well over each other, although there is a noticeable shift towards greater wavelengths as the concentration is decreased. As should be expected, the half width of the absorption band is approximately independent of concentration, but with decreasing concentration a splitting of the primary maximum into two is suspected, perhaps indicating independent absorption by two states of the complex.

Since the accuracy of the results depends not only on the limits of the apparatus, but mostly on the observer himself, the data is expected to be accurate only to about 5%, and further work to investigate this complex will be taken in hand in the near future.

Acknowledgements

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INFRARED ABSORPTION STUDY OF THE RELATION BETWEEN VISCOSITY AND INTERMOLECULAR HYDROGEN BOND FORMATION FOR SOLUTIONS OF PHENOLIC COMPOUNDS IN OILS

Part I.—Solutions of Bhilawanol in Mineral Oil

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1. Introduction

Investigations of the viscosity of mixtures of mineral oils with a series of long and short chain phenolic compounds by Qurashi and coworkers have yielded certain significant generalizations regarding the depression in viscosity that occurs in such mixtures.[1,2,3] It has been found[2,3] that the relative depression $-\Delta\nu/\nu$ for any given concentration of phenolic compound is proportional to $\nu^{0.36}$, whence it could be shown that the function $\Delta\psi_{0.36} = \Delta[(\nu^{-0.36} - 1)/0.36]$ is independent of the number of phenolic hydroxyl groups.

In order to elucidate the precise dependence of this depression on the nature of the molecule and the degree of association, it was considered desirable to undertake a quantitative study of the OH and hydrogen bond infrared absorption region in the neighbourhood of 3μ, using mixtures containing various concentrations of the phenolic compounds. The observed intensity of the absorption band depends on the one hand on the concentration of the absorbing molecules and on the other on the percentage of hydrogen bond formation, and the (peak) intensities of the resolved absorption peaks at sufficiently high resolution are mathematically correlated in the present paper with the degree of hydrogen bond formation, and thence with the viscosity depression, by using certain fundamental assumptions regarding the mechanism of the viscosity depression.

2. Experimental Details

The spectral region that is usually considered important in infrared spectrometry extends from about 2μ to 15μ, and, although infrared spectrometers used for measuring absorption spectra in this region do not differ in fundamental principles from those employed in visible and ultraviolet spectrometry, certain physical limitations of the commonly used optical materials and light sources necessitate some radical differences in design, and the best resolution is of the order of 2 to 5 cm.$^{-1}$

A Leitz automatic recording spectrometer with a prism of 15 cm. base was used in the present investigation. With the normal slit programme and a sodium chloride prism, this gives a resolution of about 11 cm.$^{-1}$ in the region of the observed OH and H-bond peaks, which resolution is sufficient for the preliminary study shown in Fig. 1(a). Because of the large aperture of the prism, it is possible to use narrower slits, down to 0.035 mm.; at this width, when using a sufficiently slow recording speed coupled with a 3:1 chart magnification, it is easy to obtain a resolution of somewhat better than 5 cm.$^{-1}$, which is ample for accurate work in the present case, as seen in Fig. 1(b). The standard recording paper is divided linearly from 2μ to 15μ (Fig.1(a)), and for high resolution measurements, the special recording arrangement extends the spectra to three times their lengths as seen from the graphs of Fig. 1(b).

The liquid samples were contained in disc-type cells with sodium chloride plates separated by spacers, whose thicknesses were chosen in order to produce accurately measurable peaks for the various concentrations. For the measurements with bhilawanol, two cell thicknesses, namely 0.033 mm. and 0.083 mm., were found suitable and were controlled by interference fringe measurements[4] with the empty cells, using the wavelength range 5 to 15μ.

3. Infrared Absorption Curves for Bhilawanol and their Analysis

An organic compound, whether aliphatic or aromatic, containing a free OH group shows a narrow symmetrical absorption band depending somewhat upon the rest of the molecule.[5] The general behaviour of the absorption characteristics of the OH band at various concentrations of bhilawanol in mineral oil is shown in Fig. 1(a). In dilute solutions, the 2.87 μ (3480 cm.$^{-1}$) band of the OH group is quite strong, while the broader band at 3.00 μ (3330 cm. -1) due to hydrogen bonding is relatively weak. As the concentration of bhilawanol increases, the relative number of associated molecules becomes greater and the 3.00 μ (3330 cm. $^{-1}$) peak becomes stronger relative to the normal OH peak. In order to make a quantitative study of the OH peak and the hydrogen bonding in detail, the spectra were taken

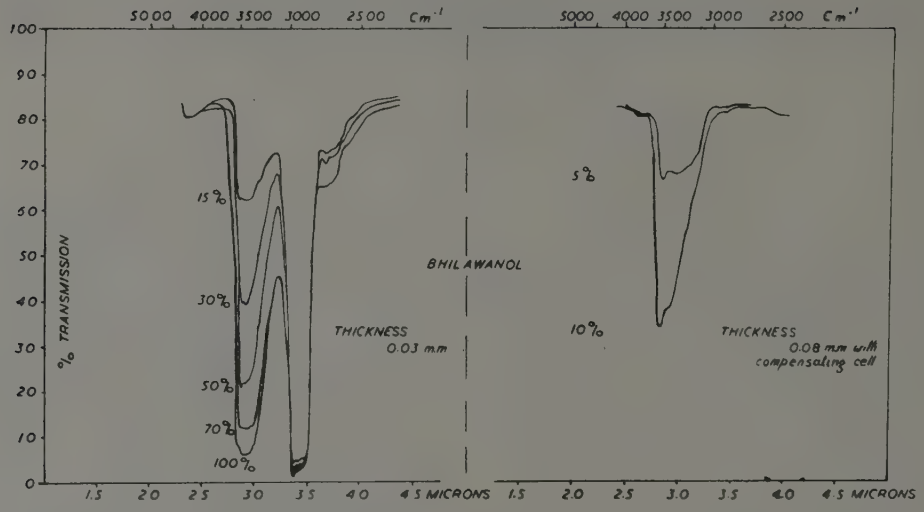

Fig. 1(a).—Preliminary infrared absorption curves in the range of 2 to 4 microns for solutions of bhilawanol in a blend of B.O.C. "90" and "60" mineral oils.

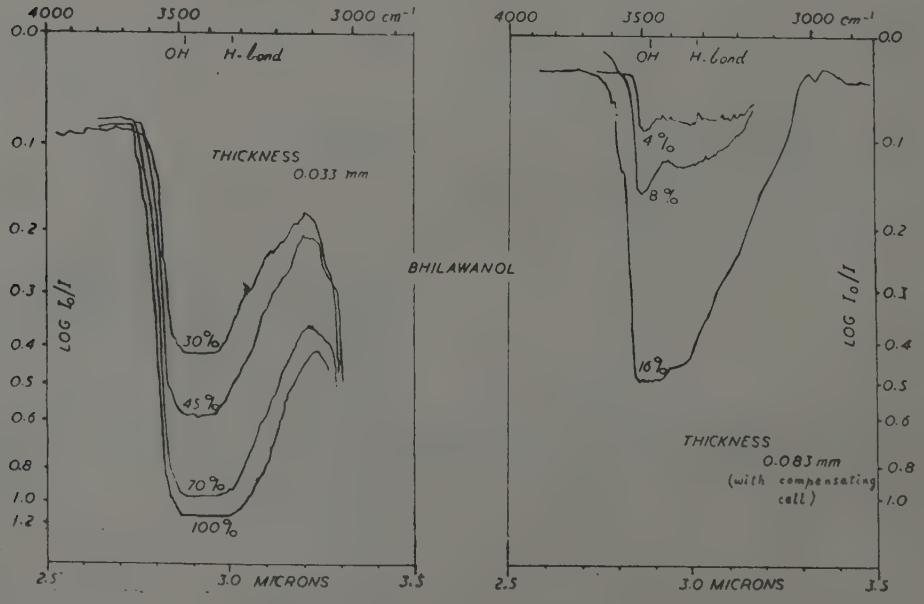

Fig. 1(b).—OH and H-bond peaks at high resolution for various concentrations of bhilawanol in the mineral oil blend.

TABLE 1.—PEAK HEIGHTS AND CALCULATED ABSORBANCES FOR THE SHARP OH PEAK AT 2.87 μ (3480 CM.$^{-1}$) IN BHILAWANOL OIL MIXTURES.

Cell thickness	% Conc. of bhilawanol (by weight =C)	Unresolved peak height (log I_0/I)	Absorbance (for 1 cm. thickness)	Corrected height (after resolution)	a=Corrected absorbance	log Conc.	log 'a'
	100	1.2	340	0.793	240	2.00	2.38
	70	0.870	264	0.495	150	1.84	2.18
0.033mm.	45	0.497	151	0.310	93.9	1.65	1.97
	30	0.346	105	0.209	63.3	1.48	1.80
	16	0.510	61.4	0.360	43.4	1.20	1.64
0.083mm.	8.0	0.160	19.3	0.130	15.7	0.90	1.20
	4.0	0.061	7.3	0.046	5.5	0.60	0.74

TABLE 2.—PEAK HEIGHTS AND CALCULATED ABSORBANCES FOR THE BROAD HYDROGEN BOND PEAK AT 3.00μ (3330 CM.$^{-1}$) IN BHILAWANOL OIL MIXTURE.

Cell thickness	% Conc. of bhilowanol (by weight) =C	Unresolved peak height (log I_0/I)	Absorbance (for 1 cm. thickness)	Corrected height(after resolution)	a= Corrected absorbance	log Conc.	log 'a'
	100	1.13	342	1.11	336	2.00	2.53
	70	0.878	267	0.855	259	1.84	2.41
0.033mm.	45	0.446	135	0.435	132	1.65	2.12
	30	0.330	100	0.310	93.9	1.48	1.97
	16	0.442	53.2	0.325	39.2	1.20	1.59
0.083mm.	8.0	0.124	14.9	0.104	12.5	0.90	1.10
	4.0	0.045	5.4	0.035	4.2	0.60	0.62

at higher resolution with expansion by a factor of three as shown in Fig. 1(b).

The intensities of the absorption bands in terms of absorbance 'a' for a 1-cm. thickness were determined from the heights of the absorbing peaks by dividing log I_0/I for the peaks by the appropriate cell thickness (in cm.). In order to eliminate errors due to overlapping of the OH and H-bond peaks, graphical resolution of the pairs was carried out: the resolved peaks are shown by thick lines in Fig. 2, and the corrected peak intensities (absorbances)were calculated afresh from these resolved peaks as shown in Tables 1 and 2.

The graphs of log 'C' against log 'a' are shown in Fig. 3, where 'C' is the concentration (by weight) and 'a' is the equivalent absorbance of a 1-cm., thickness of sample. The slope of the graph corresponding to the sharp OH peak is seen to be 1.05 $\pm$0.05, and since the number of OH groups is proportional to the concentration of bhilawanol, this indicates that the intensity of the OH peak is proportional to the concentration of OH groups. We may therefore expect that the intensity of the hydrogen bond peak will be proportional to the concentration of hydrogen bonds in the sample. Now the slope of the graph corresponding to the broad hydrogen bond peak (Fig. 3) is 1.40$\pm$0.03, thus indicating that the concentration of hydrogen bonds is proportional to the power 1.40 of the concentration of bhilawanol molecules.* This is to be compared with a theoretical estimate of 2 for the index, in case one H-bond is formed only between pairs of molecules of bhilawanol. The value 1.40 of this index would appear to indicate that hydrogen bond formation between a bhilawanol molecule and an oil molecule is about one-half as effective as that between two molecules of bhilawanol.

*It is to be noted that, although the concentrations have been taken on a weight basis, these are very close to the molar concentrations, because the molecular weights of bhilawanol and the mineral oil are nearly equal, being 316 and 340, respectively.

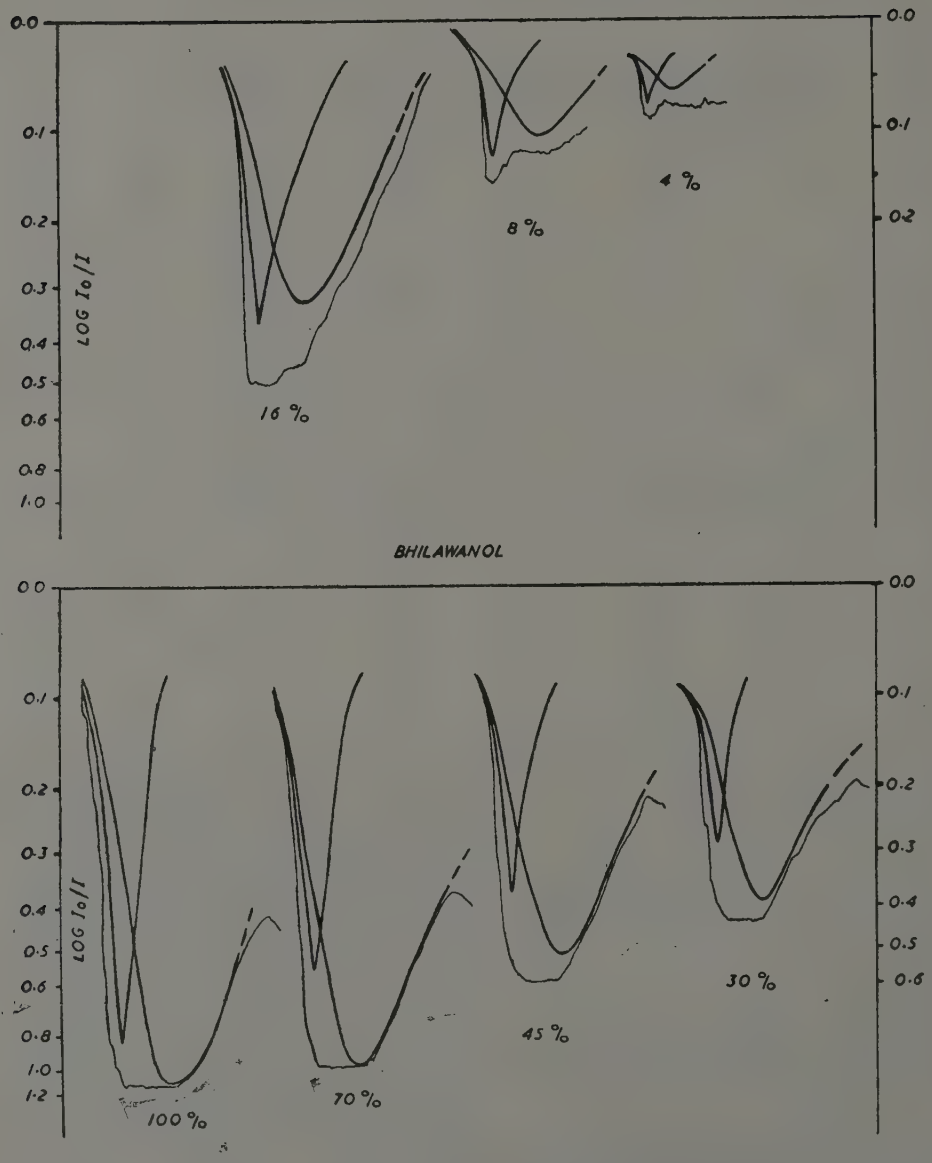

Fig. 2.—Graphical resolution of the curves of Fig. 1(b) into pairs of curves for the OH and H-bond peaks. The ordinate scale is marked in terms of the absorbance, log I_0/I.

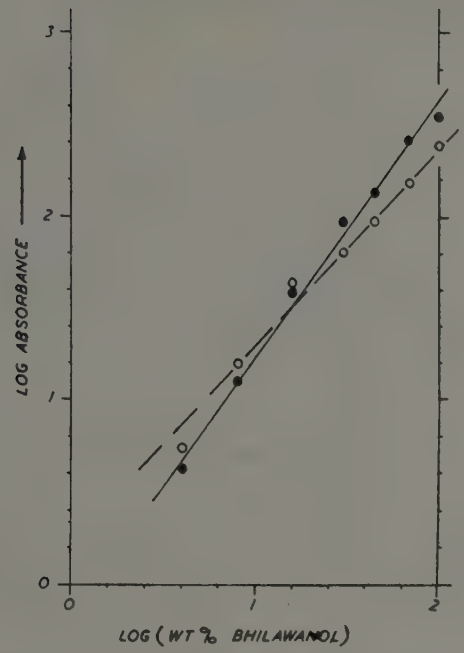

Fig. 3.—Logarithmic plots of peak absorbance (for 1 cm. layer) against weight % bhilawanol for the OH peak (hollow circles, broken line) and the H-bond peak (solid circles, full line). The scatter of the experimental points is mainly attributable to errors in the graphical resolution of peaks (Fig. 2).

4. Derivation of Formula for Comparison with Viscosity Measurements

On the basis of the data given in Table 2 and Fig. 3, we can now draw a curve showing the absorbance 'a' at the H-bond peak as a function of concentration 'C'. This graph is seen in Fig. 4, together with another graph for a/C against C. Since the OH peak intensity has been found above to be proportional to the concentration of OH groups, we concluded that the intensity of the hydrogen bond peak gives a good measure of the extent of the hydrogen bond formation for bhilawanol in mineral oil. Now, if the viscosity depression $-\Delta\nu$ produced by dilution of the bhilawanol to any concentration is due to the partial dissociation of the hydrogen bonds, we can put $-\Delta\nu/\nu$ varies as (relative change in number of hydrogen bonds per unit volume). (1)

Since $\Delta\nu << \nu$, this will be true regardless of the precise relationship between the viscosity and the hydrogen bond concentration. The change in number of hydrogen bonds is readily calculated by considering the difference between (a) the simple addition of C parts of bhilawanol to

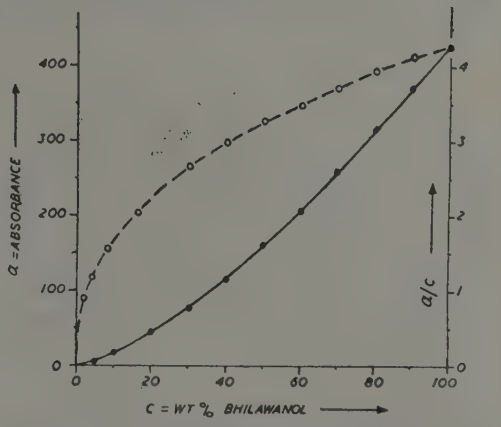

Fig. 4.—Smoothed curves (based on the linear graphs of Fig. 3) for the absorbance 'a' (full line)and for a/C (broken line) against the % concentration 'C' of bhilawanol.

(100–C) parts of oil without rupture of the hydrogen bonds, and (b) their mixing with dissemination of the molecules of these C parts over the whole volume of the mixture. In the first case, the number of the H-bonds per unit volume is proportional to $C/100 \times$ (conc. of H-bonds)$_{c=100}$, while in the second case it is porportional to (conc. of H-bonds) c%. If a_{100} is the absorbance of the H-bond peak for 100% bhilawanol, and a_c is the corresponding value for the mixture with C% bhilawanol, it follows that

$$-\frac{\Delta\nu}{\nu} = K\left(\frac{C}{100}\,a_{100} - a_c\right) \div a_{100}$$

$$= K\,\frac{C}{100}\left(1 - \frac{a_c/C}{a_{100}/100}\right) \qquad (2)$$

where K is a non-dimensional constant.

5. Application to Bhilawanol Solutions and Discussion

From Fig. 3, $\log a = 1.40 \log C - 0.17$ for bhilawanol, whence it follows that $(a_c/C) = C^{0.40}/(10)^{0.17} = 0.677\ C^{0.4}$, a graph of which is drawn in Fig. 4. The quantity, $\left[\frac{C}{100}\left(1 - \frac{a_c/C}{a_{100}/100}\right)\right]$ can be calculated from this graph (broken line in Fig. 4), and is plotted in Fig. 5(a) ,while the values of $-\Delta\nu/\nu$ actually obtained from viscosity measurements (at a temperature of 37 °C., which corresponds to that of the I.R. thermostatic chamber) are shown alongside in Fig. 5(b). The

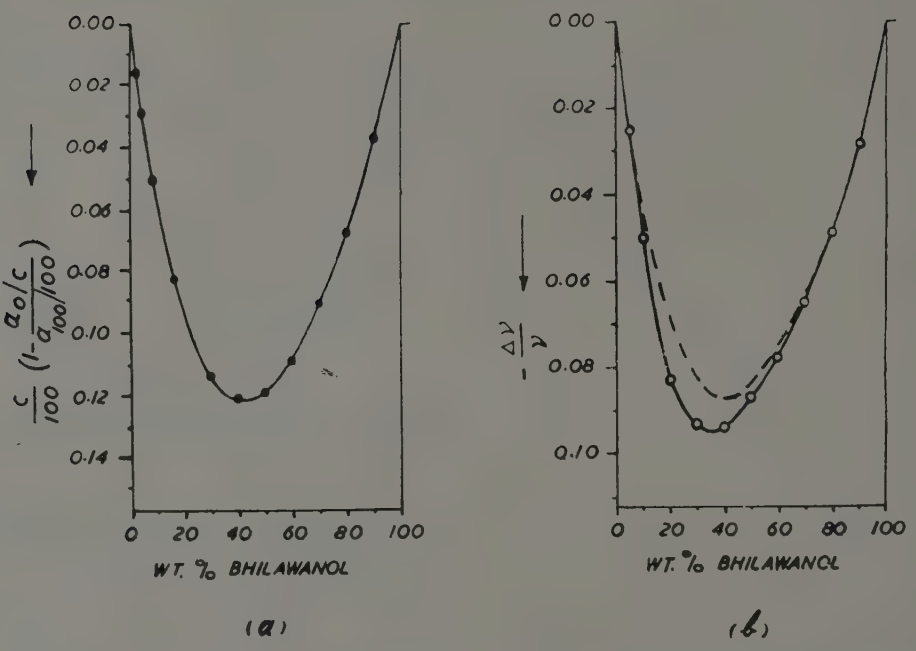

Fig. 5.—Comparison between (a) the value of $\frac{C}{100}\left(1-\frac{a_c/C}{a_{100}/100}\right)$ calculated from the infrared measurements and (b) the value of $(-\Delta\nu/\nu)$ obtained from viscosity determinations on solutions of bhilawanol.

agreement between the two curves is seen to be satisfactory (cf. broken curve), and can be brought within 5% by multiplying the scale for the calculated values by 1.07. This agreement amply justifies the basic theory leading up to the curve of Fig. 5(a). From the ratio between the finally adjusted scales of the two graphs, the *non-dimensional constant* of proportionality, K, in equation(2) comes out to be

$$K = (0.10 \pm 0.005)/0.130 = 0.77 \pm 0.04$$

Further experiments are being carried out with other phenolic compounds in order to determine to what extent K depends on the nature of the compound.

An interesting feature of the foregoing results is the fact that the right-hand side of equation (2) contains the term a_c/C, which varies as $(C/100)^{0.40}$ while the left-hand side, i.e. $-\Delta\nu/\nu$ has previously been shown[3] to vary as $\nu^{0.36}$. It is possible that a study of other phenolic compounds will lead to further elucidation of the significance of these two exponents 0.40 and 0.36.

Acknowledgements

The authors are grateful to Dr. A. Kamal for kindly providing the sample of bhilawanol, and to Dr. Salimuzzaman Siddiqui for his interest and encouragement.

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JUTE AS A FILTER FABRIC IN SUGAR MILLS

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Filtration is intended to separate solid particles from the gaseous or liquid medium in which they are suspended, either to reclaim the solids or to obtain a clear filtrate. The success of the cloth will depend upon its ability to hold back the finest particles, which it is required to separate and in its capacity to avoid becoming "blinded" for prolonged period. The ideal cloth will also need to be sufficiently permeable to allow the liquid to pass through at a reasonable rate, and to be easily cleaned, when the arrested particles have to be removed.

An experiment was conducted with a view to reducing the cost of filter medium by replacing the usual cotton twill (Fig. 1) costing Rs. 4/7/- per yard by jute canvas (Fig. 2) of Rs. 1/12/- per yard. One thousand yards of jute canvas was purchased from Peoples Jute Mills Limited, East Pakistan, and tried out at the Charsadda Sugar Mills Limited, as filter medium for cane juice.

The recovery of dissolved sugar from cane juice includes the use of filters at two stages: first in the separation of the carbonated cane juice from the insoluble impurities and lime-sludge produced when the raw juice is heated at about 55°C. and treated with milk of lime and carbon dioxide. The filter-feed (pH 10.6) usually has about 4% cake-forming solids and the resulting lime-cake is washed to a low sucrose content. The second stage consists of the separation and washing of calcium carbonate. Here the first clear juice is further carbonated to pH 8.4, heated to 70 °C. and filtered to obtain a clear second carbonated juice. Jute canvas was tried for first carbonation only, as it is the stage involving the main consumption of filter-medium in the sugar industry.

Experiments on Life of the Filter Medium

The experiment was carried out on plate and frame type filter-presses having 46 plates with a total filtering area of 626 sq. ft. and a flow rate of 12 cu. ft./mt. Double jute canvas pieces were laid over each plate of one press and the cotton twill pieces in the similar way on the other. Comparative observations taken with these filter presses are shown in Tables 1 to 3.

These observations reveal that the number of filtrations in case of cotton and jute before repairs are the same while after repairs the consumption of jute canvas has increased, i.e., under similar conditions of temperature, pressure and abrasion etc., it deteriorates earlier. It has a high absorbency as compared to cotton. When wet, it does not retain its original strength and thus cannot withstand the operational conditions for a longer period.

It is observed that juice penetration through cotton twill, which before use is flexible, coarse-

Fig. 1.—Cotton twill.

Fig. 2.—Jute canvas.

grained and porous, becomes more and more difficult after a large number of operational cycles. This is because most of silica and other fine calcium carbonate solids present in the juice are usually retained by the pores of the cotton twill. Even after washing they do not clear out but tend to blind the cloth and make it thick, stiff, hard and brittle and difficult to repair and wash. This effect of cloth plugging on filtration rate is so appreciable that it ultimately becomes the cause for the subsequent replacement of the cotton twill. Quite contrary to this, in the case of jute canvas which is thick, coarse and tough, before use, the rate of filtration ramains reasonable throughout its service. After washing, the pores do not retain silica and other particles and thus the canvas remains soft, flexible, thin, pliable and easier to repair and reuse. Both the fabrics are found to be almost equally resistant towards alkaline cane juice (pH 10.6).

Some physical characteristics of both fibres are given in Table 4.

Inspite of the higher consumption of jute canvas, yet in terms of money, the cost of cotton twill required to filter the juice obtained from 100 tons of cane is Rs. 21/12/- as compared with Rs. 10/14/- of jute canvas, i.e. jute canvas is about 50% cheaper than the cotton twill.The seasonal saving effected by use of jute fabric(on the basis of 200 days compaign at 1500 tons per day cane crushing rate, totalling 3,00,000 tons cane) comes to be as given in Table 5.

Quality of the Filtrate

Analytical data showing comparative operational efficiency of both the fabrics is given in Table 6. From this data it is found that both the filter-mediums have given the same "appreciable cake thickness". Applying the same volume of wash-water the cake has retained a somewhat lower percentage of sugar in case of jute canvas,i.e. more sugar is recovered, hence less evaporation cost. It may be due to right bridging across the pores after beginning to feed. No bleeding for longer time is observed. Further, particle-wedging into the pores does not take place as otherwise it would have greatly increased the resistance to flow. The press-efficiency w.r.t. evaporation cost and sugar left in washed lime-cake is thus high if canvas is used which retains the solids without plugging.

Taking account of the above factors, the net saving effected by use of jute canvas, assuming that 3,00,000 tons cane is crushed in a season, has been shown in Table 7.

Table 1.—Physical Nature of the Filter Medium before and after Filtration.

Particulars	Type of Medium	
	Cotton	Jute
Weave	Twill	Plain
Weight per sq. yd.	17 oz.	16 oz.
Dimension before use	78″ × 38″	80″ × 37″
Dimension after use	76″ × 38″	75″ × 37″
Shrinkage after use	2.56 %	6.25 %

Table 2.—Time Required per Operation (at about 50 lbs. p.s.i. pressure).

Operation	Cotton cloth	Jute canvas
Press filling time (from 1st cock to last cock)	6 min.	5 min.
Running time (juice filtration)	46 ,,	46 ,,
Washing time	10 ,,	8 ,,
Steaming time	5 ,,	5 ,,
Total time	67 ,,	64 ,,

Table 3.—Number of Operations Performed per Set of Filter Fabric (94 pieces) per Press.

Operation	Cotton	Jute
Before wash	30	31
After wash	35	34
After repairs	206	155
Total operations	271	220
Service duration in hours (for juice filtration only)	208	169

Table 4

Characteristics	Cotton	Jute
Sectional shape	Bean-shape	Polygonal
Specific gravity	1.52	1.48 to 1.50
Moisture regain %	8.5	12 to 13

TABLE 5

Particulars	Cotton twill	Jute canvas
Filter-medium consumed / 100 tons cane	4.9 yd.	6.2 yd.
Filter-medium required for 3,00,000 tons	14,700 yd.	18,600 yd.
Total cost of medium required	Rs. 65,231	Rs. 32,550
Tailoring charges	Rs. 1,029	Rs. 1,581
Total cost incurred	Rs. 66,260	Rs. 34,131
Saving	Rs. 32,129	

TABLE 6.—COMPARATIVE OPERATIONAL EFFICIENCY.

Particulars	Cotton twill	Jute canvas
Thickness of cake ..	1.25″	1.25″
Moisture % cake ..	49.16	48.60
Pol % cake ..	0.80	0.60
Wash-water used ..	54 cu.ft.	54 cu. ft.
Brix of sweet water ..	2.75	2.67
Pol % sweet water ..	2.00	1.99

TABLE 7

Particulars	Cotton twill	Jute
Press-cake % cane	8	8
Total cake for 3,00,000 tons cane	24000 tons	24000 tons
Total sugar lost for 24,000 tons cake	192 tons	144 tons
Price of sugar @ Rs. 816/10/6 per ton	Rs. 1,56,798	Rs. 1,17,599
Saving per season in sugar	Rs. 39,199	
Saving per season in filter-medium cost	Rs. 32,129	
Total saving in a season	Rs. 71,328	

The clarity of the filtered juice remains somewhat low at the outset of filtration with a new jute canvas but afterwards, i.e. throughout the use of canvas, the clarity remains almost as high as that obtained with cotton twill.

Discussion

The experiments described above have shown that the use of jute canvas to replace cotton twill: as a filter medium is advantageous in two ways (a) by directly reducing the overall expenditure on the filter medium by 50%, and (b) by giving a higher sugar concentration in the filtrate.

On the other hand, the main drawback in using the jute canvas as filter-fabric is that the press-cake sticks to the outer surface of the canvas due to hairy fibres and thus cake removal process is rendered difficult, taking more time and affecting the press-capacity. Further, the holes through which juice and water is made to pass widens and loosens due to separation of fibres, and earlier failure at the edges where it serves as a gasket between plate and frame affects durability to a greater extent. This requires improvement in its manufacture. Because of these difficulties, jute canvas in its present form can be best used as a "backing" for the cotton twill.

To popularise jute canvas as a filter fabric, the jute manufacturers must produce special type of less absorbing and more heat-resistant canvas of requisite specifications for filtration in sugar industry. A balance must be struck between as open a weave as possible in order to reduce plugging, and as tight a weave as is necessary to prevent excessive "bleeding" of fine particles. The surface must be smooth for easy discharge of cake. Jute canvas in its improved form may then be successfully used for a wide range of filtration processes in several other industries and may achieve considerable economies in respect of time and money as compared with cotton and other synthetic fabrics.

If the manufacturers prepare a fabric specifically designed to suit the type of process involved, it will enable them to create a new market for this economical industrial fabric.

Acknowledgement

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THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part III.—Accurate Measurements of the Temperature Dependence of the Activation Energy of Viscous Flow in Ethylene Glycol*

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Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

1. Introduction

The nature of the connection between the viscosity of hydroxylic and other associated liquids and the molecular structure existing within these liquids has been the subject of detailed investigation in the Central Laboratories.[1–4] In previous communications,[3,4] some preliminary results were presented on the temperature variation of the viscosities of mineral oils and of glycerol and ethylene glycol, and graphs showing the activation energy of viscous flow as a function of temperature were obtained. These graphs for glycerol and glycol are reproduced in Fig. 1, and they indicate that in each case the variation of the energy E, occurs in a series of approximately equal step-like segments, the width and depth of which appear to be characteristic of each liquid. Moreover, the corresponding curves for ln 1/A, where A is the concentration factor in the Andrade equation $\eta = A \exp (E/RT)$, show steps whose depths may conceivably be interpreted as whole numbers (2 and 4) governing the size of the molecular aggregates, as appears from Eyring's interpretation of A as h/(volume of one unit of flow). However, the measurements with ethylene glycol were handicapped by the fact that the experimental error was sometimes as much as a quarter of the magnitude of the above effects. It was therefore considered desirable (a) to decrease this experimental error as much as possible, and (b) to take measurements with a smaller temperature interval ΔT between successive readings, so as to examine the variation of E within each segment, which extends over nearly 13°C. in the case of ethylene glycol. As pointed out at the end of Part II of this series of papers,[4] both these desiderata can be achieved by using a Beckmann differential thermometer and a good stop-watch capable of being read to a fiftieth of a second. The activation energy, E, can then be measured over intervals of 2.5°C., with an accuracy approaching 0.2%. In the present communication, results obtained with this improved technique are presented for the case of ethylene glycol between the temperatures of 40°C. and 120°C. A connection between the variations of E and ln 1/A is also derived.

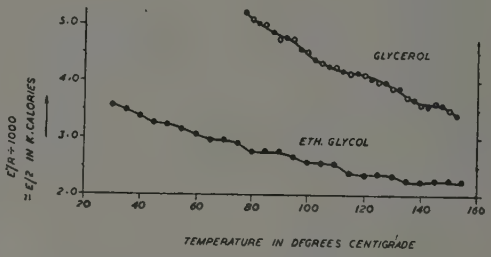

Fig. 1.—Preliminary measurements showing the temperature dependence of activation energy of viscous flow for glycerol and ethylene glycol (from Part II, Figs. 4 and 5).

2. Experimental Details and Estimation of Corrections

(a) The usual type of Beckmann thermometer has a six-degree scale, graduated in hundredths of a degree, so that readings can be taken to 0.001°C. with the help of a magnifying thermometer reader. It was found preferable not to use the last half-degree at each end, and to work with two 2.5°C. intervals from 0.5 to 3.0 and 3.0 to 5.5 scale degrees. This arrangement gives us 5 to 6 experimental points for each of the segments, and has the added advantage that the calibration corrections to the Beckmann scale are equal and opposite for successive intervals, so that the means of successive points in the graph for energy against temperature will be independent of this calibration error. With the particular thermometer used in the present experiments, this error was found to be $\pm 0.001{,}5$°C. for the two intervals of 2.5°C., which can be ignored, since the individual temperatures are read to 0.001°C. and the probable observational error in ΔT is therefore 0.001,4°C. However, a small residual correction for the value of the mean Beckmann degree remains outstanding, and is found from the expansion of mercury to be as follows:

Temperature (°C.)	0	50	100	150
Size of Beckmann degree (°C.)	0.996	0.998	1.000	1.002

*This communication is based on a thesis presented by Abdul Rauf for the degree of M.Sc. to the University of Karachi.

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(b) There is now the problem of attaining an equivalent percentage accuracy in the measurement of $\Delta \ln \nu \simeq \Delta \ln t$.

If $\bar{t} = 1/2\ (t_1 + t_2)$, and $\Delta t = t_2 - t_1$, then

$$\Delta \ln t = \ln t_2 - \ln t_1 = \ln \frac{t_2}{\bar{t}} - \ln \frac{t_1}{\bar{t}}$$

$$= \ln \left(1 + \frac{\Delta t}{2\bar{t}}\right) - \ln \left(1 - \frac{\Delta t}{2\bar{t}}\right)$$

$$= 2\left(\frac{\Delta t}{2\bar{t}} + \frac{1}{3}\left(\frac{\Delta t}{2\bar{t}}\right)^3 + \cdots\cdots\right)$$

$$= \frac{\Delta t}{\bar{t}}\left(1 + \frac{1}{12}\left(\frac{\Delta t}{\bar{t}}\right)^2 + \cdots\cdots\right), \quad (1)$$

which shows that the percentage accuracy of $\Delta \ln t$ is equal to that of Δt. The result (1) is especially useful in our calculations for $\Delta \ln \nu / \Delta T$ because the term $1/12\ (\Delta t/\bar{t})^2$ is always very small and often negligible as $\Delta t/\bar{t}$ is of the order of 0.1 in the experiments described here, e.g. from $E/R \sim -T^2\ \Delta \ln \nu / \Delta T$, we get $\Delta t/\bar{t} = 0.08$ for $T = 350°K$, $(E/R)/1000 = 4$, and $\Delta T = 2.5\,°C$.

It is now clear from equation (1) that, in order to attain an accuracy of 0.2% in $\Delta \ln t$, i.e. $(t_2 - t_1)/\bar{t}$, we must measure t_1 and t_2 to an accuracy of $1/\sqrt{2} \times 0.08 \times 0.2\%$, i.e. 1 part in 8,000, for which a good stop-watch, readable to 0.02 second, must be used because the times of flow will be of the order of 100 seconds. Further, the mean of several measurements of flow time should be taken in order to eliminate the effect of personal error, which may amount to 0.05 second in a single measurement. It will also be necessary to make corrections for the kinetic energy of flow and for the variation of liquid level in the viscometer. In Part I (Appendix II) the following equation was developed[3]

$$-\frac{\Delta \ln \nu}{\Delta T} = -\left(\frac{\ln t_2 - \ln t_1}{T_2 - T_1}\right)\left(1 + 2\,\frac{B/A}{\bar{t}^2}\right) + \frac{\alpha}{100}\,\frac{x_2 - x_1}{T_2 - T_1} \quad (2)$$

where t_1 and t_2 are the times of flow at temperatures T_1 and T_2, respectively, and x_1 and x_2 are the corresponding heights of the liquid level above the fiducial mark of the large viscometer bulb. A and B are the constants in the equation $\nu = At - B/t$, while α is the percent increase in flow time for $x = 1$ cm., and is usually a little less than unity for the British standard pattern of U-tube viscometer. Thus if $T_2 - T_1 = 2.5\,°C.$, and an accuracy of 0.2% is aimed at in $\Delta \ln \nu / \Delta T$ (~ 0.03), the measurement of x_1 and x_2 should be accurate to $0.03 \times \frac{2.5}{\sqrt{2}} \times 0.2$ cm., i.e. 0.1 mm. The correction for the changing level varies very slowly with temperature, and it is sufficient to measure the rise in level produced during a 20 °C. rise in temperature and thence to estimate the correction for a 2.5 °C. temperature difference. A mean value of 0.08 cm. rise for $\Delta T = 2.5\,°C.$ was obtained with the viscometers used in the present set of experiments.

In equation (2), the term $\Delta \ln t / \Delta T \times 2\,\frac{B/A}{t^2}$, which corresponds to the kinetic energy correction, is very small, its magnitude being of the order of $0.000{,}3 \pm 0.0001$ for the readings taken with viscometer No. 2, and about 0.000,05 for those taken with viscometer No. 1, which amount to somewhat less than 1% and 0.3% respectively of the measured quantity, $-\Delta \ln \nu / \Delta T$, and have a very small variation with temperature. Since most of the measurements described in this communication were made with viscometer No. 1, the kinetic energy correction can be neglected.

(c) The correction to be made for measuring ν in place of η was also derived in Part I (Appendix II)[3] as

$$E/R = -T^2 \Delta \ln \eta / \Delta T = -T^2 \Delta \ln \nu / \Delta T + T^2 \beta, \quad (3)$$

where $\beta = -(d\rho/dT)/\rho$, and can be determined from the coefficient of dilatation of the experimental liquid. For ethylene glycol, the International Critical Tables give the standard formula,

$$\rho_t = 1.1257 - 0.5713 \times 10^{-3}\, t - 2.766 \times 10^{-6}\, t^2 + 10.9 \times 10^{-9}\, t^3 \cdots\cdots \quad (4)$$

which is correct to within 0.001 in the range 0 °C. to 136 °C. Differentiation gives

$$-10^3 d\rho/dt = 0.5713 + 2 \times 2.766 \times 10^{-3}\, t - 3 \times 10.9 \times 10^{-6}\, t2, \quad (5)$$

whence β is readily calculated. Table 1 gives the values of ρ, β, and $T^2\beta$, calculated at intervals

TABLE 1.—CORRECTION FOR DILATATION OF GLYCOL.

Temperature (C.)	20	40	60	80	100	120
Density ρ g./ml.	1.113	1.099	1.084	1.068	1.052	1·036
$1000 \times \beta$	0.601	0.673	0.724	0.753	0.758	0.739
T2 β/1000	0.052	0.066	0.080	0.094	0.105	0.114

of 20°C. from 20°C. upto 120°C. from which the correction $T^2\beta/1000$ appears to be quite significant at the higher temperatures.

(d) A special precaution for all experimental work with ethylene glycol is the use of water-free material and the prevention of subsequent moisture absorption. Pure ethylene glycol (supplied by Griffin and Tatlock) was first redistilled under a pressure of 25 mm. of mercury, only the fraction coming over at 108°C. to 109°C., being accepted, after which the distillate was dried in vacuum over sulphuric acid and stored in a vacuum desiccator. For transferring the glycol into the viscometer with a minimum uptake of moisture from the atmosphere, the special pipette shown in Fig.2(a) was constructed, having a stop-cock and drying tube attached to its upper end. The pipette was first flushed with dry air by gently pumping air into it through the drying tube and then glycol

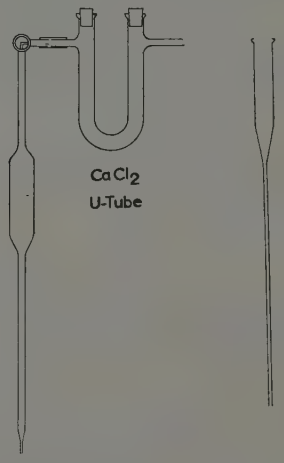

Fig. 2(a).—Pipette with stop-cock and drying tube attached and the capillary for filling the viscometer.

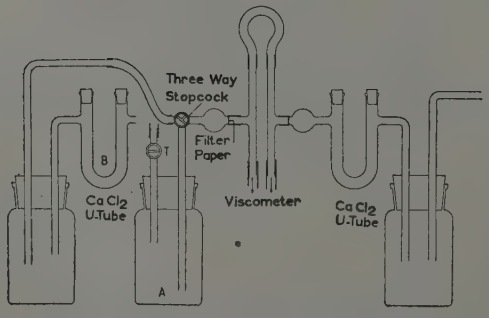

Fig. 2(b).—System of drying tubes, cocks, and ballast bottle for operating the viscometer without the entry of moist air.

was sucked into the pipette. The required volume of glycol was run into the viscometer, which had drying tubes, stop-cocks, and a ballast bottle A attached to it as shown in Fig. 2(b). The ballast bottle and the cocks are used to control the sucking up of the liquid in the capillary limb of the viscometer, as described[4] in Part II of this paper, the three-way stop-cock serving to connect this capillary limb either with A, the ballast bottle (in which a slight vacuum is previously created by suction, after which the cock T on the bottle is closed), or with B, the drying tube, whose other end is open to the atmosphere.

3. The First Series of Measurements

The viscometer was supported vertically inside an electrically heated glycerine bath[3] (Part I, Fig. 2) whose temperature could be controlled to within 0.002°C. by means of an automatic glycerine-filled control thermometer, provided that large fluctuations of mains voltage were compensated manually. The temperature range from 40°C. to 120°C. was covered in two stages of about 40°C. each, with an overlap of a few degrees near 80°C. In this first set of measurements, a British standard U-tube viscometer No. 2 (constant = 0.056) was used for the range of 40°C. to 80°C. and viscometer No. 1 for the higher temperature range in order to obtain sufficiently long times of flow. The viscometer was carefully filled (by means of a tube drawn into a capillary, Fig. 2(a), so as to avoid wetting the viscometer tube above the main bulb) and the volume of glycol was adjusted so that at the starting temperature (42.5°C. in the first set) the level was about 3 mm. below the fiducial mark on the tube immediately above the bulb, in order to allow for expansion of the glycol with rise of temperature.

The glycol having been completely enclosed in the viscometer with its system of drying tubes, the temperature of the bath was adjusted manually to within a few tenths of a degree, and then the Beckmann thermometer was adjusted to read nearly 5.5 degrees (minus) when placed in the bath. The automatic temperature control was then set to maintain the Beckmann reading steady at some value within 0.02 of 5.50° when the temperature had remained steady for nearly twenty minutes, five successive readings of the time of flow were taken with a calibrated stop-watch, the Beckmann reading being noted at regular intervals of 20 seconds during the flow. The means of the flow times as well as of the Beckmann readings were recorded, together with their respective standard deviations. The temperature was then raised until the Beckmann reading corresponded to 3.00, and the foregoing set of

measurements were repeated at this temperature, and then in the same way flow times were recorded for a reading of 0.50. The laft-hand half of Table 2(a) shows these readings for a mean Beckmann reading of 3.012, while the right-hand half shows the corresponding measurements taken during the cooling of the bath as described below. The bath temperature was raised about 0.5°C. (so that the Beckmann reading was nearly 0.00), maintained at this value for a few minutes, and then lowered successively to 0.50, 3.00 and 5.50 at each of which temperatures, the flow times and Beckmann readings were recorded as before.

It is seen from Table 2(a) that (i) the temperature fluctuation is of the order of ±0.003°C., (ii) the mean temperature during any one flow period, being obtained from seven readings, should be accurate to better than 0.001°C., and (iii) the standard error of the mean time of flow for five observations is of the order of 0.03 seconds, which corresponds to an accuracy of 1 part in 4000. This is slightly short of the accuracy aimed at, and therefore this viscometer (No. 2) was used for the lower temperature range in the first set of experiments only, while viscometer No. 1 (which gives flow times ten times as long) was used for all succeeding measurements. Table 2(b) gives the overall mean values of the flow times and the Beckmann readings over the first 5 degree interval together with the calculated values of $-T^2(\Delta \ln t/\Delta T)/1000 = (E'/R)/1000$. The table shows satisfactory agreement between the values of this quantity obtained during the heating and cooling of the bath, the standard deviations of the final means being about ±0.012, which corrresponds to an accuracy of 0.3%.

The results obtained from the first series of experiments are shown in Table 3, the range from 76°C. to 120°C. having been covered with fresh sample of glycol in viscometer No. 1. Two facts about the values calculated for $(E'/R)/1000$ are noteworthy: (1) the standard deviation of the means obtained from the measurements with rising and falling temperatures in the lower temperature range is nearly 0.015, and (2) there is a systematic tendency at temperatures above 75°C. for the value under the heading "temperature rising" to be higher than the corresponding value under the heading "temperature falling", the magnitude of the difference rising from 0.02 for 75°C. upto 0.16 for 110°C. (inset to Fig. 3). This difference is attributable to the gradual loss of glycol by evaporation, but, due to the symmetrical mode of taking observations with rising and falling temperatures, the means of corresponding values in the two columns will be substantially independent of the error due to this cause. These mean values are plotted against temperature as the upper graph in Fig. 3, and they confirm the presence of step-like segments previously observed in the preliminary measurements shown in Fig. 1. The scatter of the points is nearly ±0.02, which is in reasonable agreement with

TABLE 2(a).—TYPICAL SET OF MEASUREMENTS WITH VISCOMETER No. 2 AT 44.85°C.

Temperature rising			Temperature falling		
Time elapsed since commencement (secs.)	Reading on Beckmann thermometer	Time of flow	Time elapsed since commencement (secs.)	Reading on Beckman thermometer	Time of flow
0	3.014		0	3.003	
20	3.019		20	3.001	
40	3.021		40	3.006	
60	3.023		60	3.010	
80	3.020		80	3.005	
100	3.020		100	3.005	
120	3.020		120	3.004	
Mean	=3.020	2′ 12.94″	Mean	=3.005	2′ 12.94″
0	3.010		0	3.005	
20	3.000		20	3.010	
40	3.003		40	3.016	
60	3.005		60	3.020	
80	2.998		80	3.021	
100	2.999		100	3.022	
120	2.992		120	3.026	
Mean	=3.001	2′ 12.80″	Mean	=3.017	2′ 12.90″
0	3.020		0	3.010	
20	3.020		20	3.012	
40	3.013		40	3.020	
60	3.004		60	3.023	
80	3.002		80	3.025	
100	3.001		100	3.027	
120	3.000		120	3.024	
Mean	=3.009	2′ 13.06″	Mean	=3.020	2′ 12.90″
0	3.015		0	3.021	
20	3.017		20	3.030	
40	3.020		40	3.030	
60	3.014		60	3.029	
80	3.014		80	3.027	
100	3.012		100	3.015	
120	3.012		120	3.007	
Mean	=3.015	2′ 12.92″	Mean	=3.023	2′ 12.86″
0	3.017		0	3.004	
20	3.017		20	3.006	
40	3.018		40	3.012	
60	3.018		60	3.020	
80	3.013		80	3.026	
100	3.016		100	3.010	
120	3.014		120	3.010	
Mean	=3.106	2′ 12.98″	Mean	=3.013	2′ 12.90″
Overall means	3.012 ±0.003	2′ 12.94″ ±0.04″	Overall means	3.016 ±0.003	2′ 12.90″ ±0.01″
Temperature of bath = 44.85°C.			Temperature of bath=44.85°C.		

TABLE 2(b).—CALCULATIONS FOR THE VALUES OF $\left(-\frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T}\right)$ AT 43.6 °C. AND 46.1 °C.

	Mean Beckmann reading	Mean time of flow (secs.)	$T_1 - T_2 = \Delta T$	$t_1 - t_2 = -\Delta t$	$-\frac{\Delta \ln t}{\Delta T} \times 100$	Mean temperature °C.	$-\frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T}$	Mean of values for heating and cooling sequences
Heating sequence	5.499±0.002	143.98±0.04	2.487	11.04±0.06	3.206±.017	43.6_1	3.214±.018	3.208±0.008
	3.012±0.003	132.94±0.04	2.488	9.88±0.06	3.104±.018	46.1_0	3.160±.018	
	0.524±0.001	123.06±0.05						
Cooling sequence	5.510±0.002	143.93±0.04	2.494	11.03±0.04	3.196±.012	43.6_0	3.203±.012	3.182±0.016
	3.016±0.003	132.90±0.01	2.502	10.06±0.04	3.146±.012	46.1_0	3.203±.012	
	0.514±0.002	122.84±0.04						

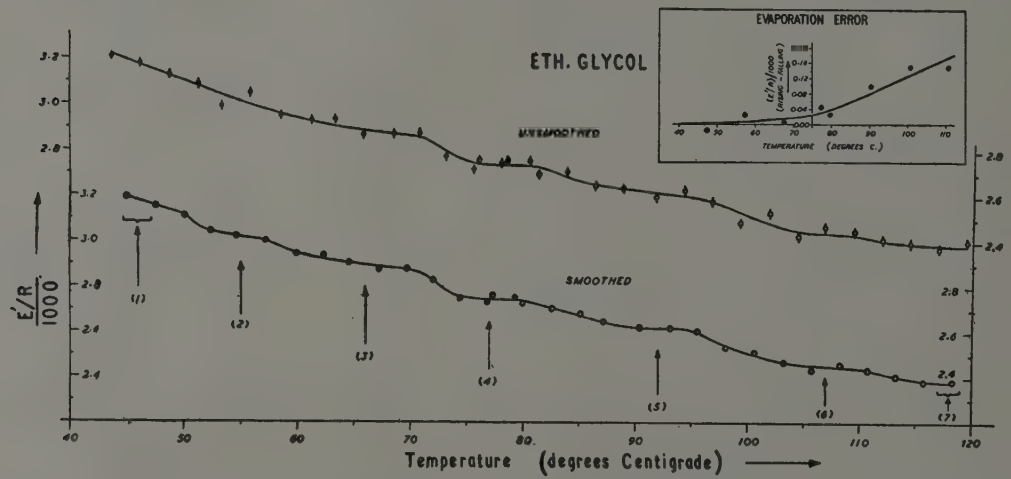

Fig. 3.—First series of results for the temperature variation of (E′/R)/1000 for ethylene glycol: upper graph; unsmoothed ;lower graph, smoothed; inset, dependence of evaporation error on temperature.

the estimates of random error obtained from Table 3 and the inset to Fig. 3. In order to decrease the scatter still further, smoothed values of $\frac{E'/R}{1000} = -\frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T}$ have been calculated in Table 3 by taking the means of experimental values at successive temperatures, and these smoothed values are plotted in the lower graph of Fig. 3, which brings out the regular recurrence of the steps more clearly than does the upper graph. However, the process of smoothing obscures the detail present in intervals of less than 5 °C., and therefore it was considered preferable to increase the accuracy by repeating the whole series of measurements over the range 40 °C. to 120 °C. Such a repetition would also serve as a check on the reproducibility of the steps observed in the curve.

4. Second Series of Measurements

Fresh samples of redistilled ethylene glycol were used, and the values of (E′/R)/1000 obtained from this second set of measurements are given in Table 4(a) alongside of the corresponding values from the first series. The standard deviations for the second set were found to be about two-thirds

TABLE 3.—VALUES OF (E'/R)/1000 OBTAINED FROM THE FIRST SERIES OF MEASUREMENTS.

Mean temperature (°C)	$\frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T} = \frac{E'/R}{1000}$ temperature rising	temperature falling	Mean	Smoothed $\frac{E'/R}{1000}$	Mean temperature (°C)	$-\frac{T^2}{1000}\frac{\Delta \ln t}{\Delta T} = \frac{E'/R}{1000}$ Tempera-ture rising	Temperature falling	Mean	Smoothed $\frac{E'/R}{1000}$
43.60	3.214	3.203	3.208± 8		76.10	2.776	2.760	2.768± 8	
				3.195					2.766
46.10	3.160	3.203	3.182±16		78.55	2.773	2.756	2.764±10	
				3.156					2.736
48.73	3.136	3.125	3.130± 9		81.33	2.762	2.656	2.709±15	
				3.112					2.713
51.20	3.071	3.115	3.093±17		83.83	2.754	2.680	2.717± 7	
				3.044					2.686
53.30	3.024	2.966	2.995±21		86.40	2.721	2.592	2.656±16	
				3.022					2.650
55.75	3.081	3.018	3.050±22		88.90	2.669	2.619	2.644± 8	
				3.000					2.624
58.53	2.965	2.936	2.951±13		91.86	2.661	2.546	2.604±10	
				2.944					2.620
61.15	2.919	2.956	2.938±14		94.36	2.689	2.585	2.637± 7	
				2.942					2.610
63.33	2.987	2.903	2.945±25		96.82	2.643	2.525	2.584± 8	
				2.910					2.538
65.83	2.883	2.865	2.874±10		99.33	2.571	2.415	2.493±14	
				2.879					2·515
68.47	2.895	2.874	2.884±10		101.98	2.640	2.434	2.537±22	
				2.884					2.484
70.85	2.888	2.882	2.885±15		104.51	2.492	2.370	2.431±10	
				2.834					2.452
73.13	2.835	2.734	2.784±30		106.93	2.562	2.381	2.472±11	
				2.754					2.462
75.57	2.690	2.760	2.725±35		109.51	2.519	2.386	2.452±12	
				2.740					2.438
78.00	2.797	2.713	2.755±26		111.95	2.545	2.301	2.423±19	
				2.760					2.412
80.55	2.807	2.722	2.764±25		114.45	2.532	2.268	2.400±21	
									2.387
					116.97	2.455	2.293	2.374±14	
									2.390
					119.50	2.498	2.312	2.405±15	

NOTE.—The standard deviations have been obtained as the means of two estimates, namely the errors in time and temperature measurements and the differences between measurements made with rising and falling temperature sequences (with allowance for evaporation error in the higher temperature range).

of those for the first set, which is partly due to the use of viscometer No. 1 throughout, and partly to an improvement in technique consequent upon practice. The degree of agreement between the results of the two sequences of measurements is consistent with their separate standard errors, when account is taken of the systematic defect of 0.02 to 0.04 due to the larger kinetic energy correction for viscometer No. 2, which was used in the lower temperature range for the first series. The data obtained from the second series of measurements are plotted in Fig. 4, the smoothed graph in which is seen to agree remarkably well with the corresponding (smoothed) graph in Fig. 3. A comparison of the temperatures at the middle of the flat parts of the successive steps is made in Table 4(b) for the two series of measurements, and shows agreement to within 1.5°C., thus providing an excellent confirmation of the reproducibility of the experimental data. The mean interval between successive steps is found to be $11.2° \pm 0.7°C$.

TABLE 4(a).—COMPARATIVE TABLE OF VALUES OF (E′/R)/1000 OBTAINED FROM THE TWO SERIES OF MEASUREMENTS.

Second series Temp.	Second series E′/R / 1000	First series Temp.	First series E′/R / 1000	Overall mean Temp.	Overall mean E′/R / 1000	Total correction
40.45	3.264			40.45	(3.264)	0.090
42.95	3.252	43.60	3.208	43.3	3.230	
46.01	3.199	46.10	3.182	46.05	3.190	
48.51	3.186	48.73	3.130	48.6	3.158	
50.80	3.158	51.20	3.093	51.0	3.126	0.095
53.40	3.052	53.30	2.995	53.35	3.024	
56.04	3.051	55.75	3050	55.9	3.050	
58.54	3.102	58.53	2.951	58.55	3.026	
61.16	2.973	61.15	2.938	61.15	2.956	0.100
63.65	2.865	63.33	2.945	63.5	2.905	
66.37	2.959	65.83	2.874	65.6	2.916	
68.88	2.898	68.47	2.884	68.7	2.891	
71.38	2.853	70.85	2.885	71.1	2.874	0.105
73.87	2.834	73.13	2.784	73.5	2.809	
76.25	2.771	75.57	2.725	75·9	2.748	
78.75	2.735	78.00	2.755	78.4	2.745	
—	—	80.55	2.764	80.55	(2.764)	0.110

Second series Temp.	Second series E′/R / 1000	First series Temp.	First series E′/R / 1000	Overall mean Temp.	Overall mean E′/R / 1000	Total correction
78.02	2.776	76.10	2.768	77.05	2.772	0.095
80.42	2.758	78.55	2.764	79.5	2.761	
		81.33	2.709	80.9	2.734	
83.67	2.717	83.83	2.717	83.75	2.717	
86.18	2.694	86.40	2.656	86.3	2.675	0.095
88.96	2.641	88.90	2.644	88.95	2.642	
91.45	2.671	91.86	2.604	91.65	2.638	
94.34	2.601	94.36	2.637	94.35	2.619	
96.87	2.609	96.82	2.584	96.85	2.596	0.100
99.66	2.524	99.33	2.493	99.5	2.508	
				100.7	2.515	
102.1	*	101.98	2.537			
				103.2	2.484	
104.66	2.540	104.51	2.431	104.6	2.486	
107.21	2.464	106.93	2.472	107.05	2.468	0.105
110.36	2.471	109.51	2.452	109.95	2.462	
112.90	2.473	111.95	2.423	112.4	2.448	
116.10	*	114.45	2.400			
				115.7	2.387	
118.67	*	116.97	2.374			0.110
				118.25	2.390	
		119.50	2.405			

*The measurements at 102°C. was accidentally missed out, while those at 116.1°C. and 118.7°C. were rejected because a particle had found its way into the liquid in the viscometer.

TABLE 4 (b).—COMPARISON OF TEMPERATURES AT MIDDLE OF FLAT PART OF STEPS IN THE TWO SERIES OF MEASUREMENTS.

Ordinal No. of step	1	2	3	4	5	6
Temperature from 1st series (°C.)	47·5	56	66.5	79·5	93	104
Temperature from 2nd series (°C.)	47·5	57	66.5	80	91·5	102·5
Mean (°C.)	47·5	56·5	66.5	79.8	92.2	103.2
First Differences (°C.) ..		9.0	10.0	13·3	12.4	11.0

TABLE 5.—MEAN VALUES OF $\frac{E'/R}{1000}$ AND TEMPERATURE AT THE MIDDLE OF THE FLAT PORTIONS OF THE STEPS.

Ordinal No. of flat	1	2	3	4	5	6	7
$\frac{E'/R}{1000}$ for flat ..	3·19	3.04_0	2.90_0	2.75_2	2.63_2	2.46_8	2.37_5
Correction ..	0.090	0.095	0.100	0.100	0.100	0.105	0.110
T_m = Temperature at middle of flat (°C).	46.0	55·5	66.5	78.5	92.0	106.5	~ 119

The mean value of (E′/R)/1000 at corresponding temperatures in the two series of measurements can now be taken. These means are also given in Table 4(a) and are plotted in the upper curve of Fig. 5, in which the hollow circles are for the high temperature range, and the four crosses correspond to points taken from the smoothed values of Table 3, due to the accidental non-availability of the corresponding observations in the second series of measurements. The mean graph brings out the

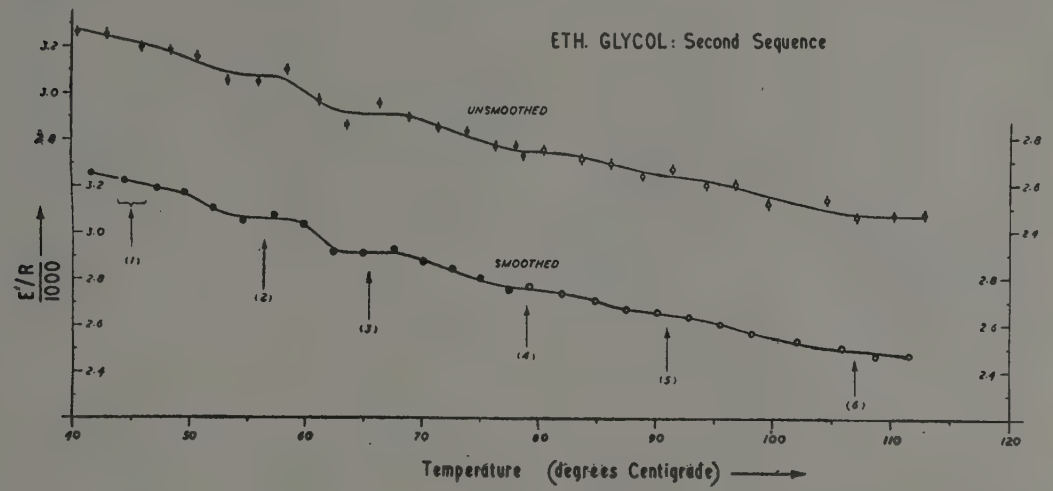

Fig. 4.—Graphs of second sequence of measurements of (E′/R)/1000 for ethylene glycol: upper graph; unsmoothed; lower graph smoothed.

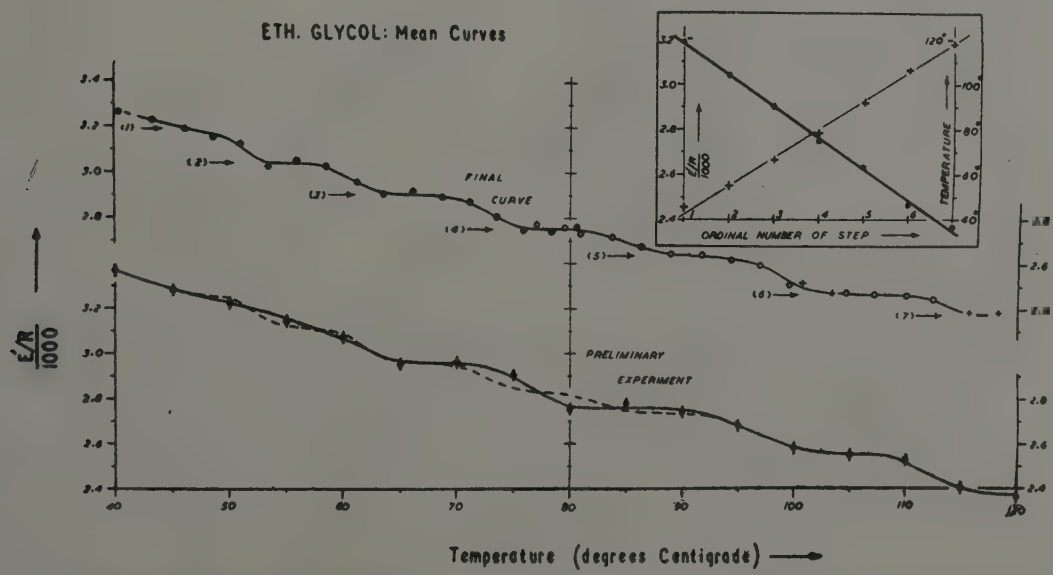

Fig. 5.—Mean curve for (E′/R)/1000 (upper graph) compared with the preliminary data of Fig. 1 (lower graph), the standard errors being indicated by the radii of the circles in the upper graph and by the short vertical lines in the lower graph. The inset shows plots of (E′/R)/1000 and of temperature at the middle of the flats against the ordinal number of the step.

regularity of the steps very well, the r.m.s. scatter of the points about the graph being only 0.014, while the average height of the steps is nearly 0.14 units of (E′/R)/1000, i.e. ten times as great. Detailed comparison of the steps with the corresponding portion of the graph obtained from the preliminary data of Fig. 1 (re-plotted in the lower part of Fig. 5, the short vertical lines representing the estimated standard deviations) shows discrepancies only in the neighbourhood of 57°C. and 77°C. Both of these can, however, be removed by drawing the preliminary curve as indicated by the broken line, which is still consistent with the known standard error of ± 0.025 unit in the plotted points. It is clear that the upper graph represents a considerable improvement in two different ways: (a) the standard deviation has been decreased by a factor of two, and (b) twice as many experimental points have been obtained with half the previous measuring interval of temperature.

5. Discussion of the Characteristics of the Steps

In Table 5 are collected the data on the flat portions of the steps as obained from the upper graph of Fig. 5. These data are plotted in the inset to Fig. 5, and they provide evidence for the constancy of the interval between successive steps with regard to both energy and temperature. The mean corrected energy interval $\Delta E/R$ is found to be $0.138 - 0.004 \pm 0.009$, and the mean temperature interval is 12.1 ± 0.7°C. (cf. the value of $11.2° \pm 0.7$°C. obtained from Table 4(b)). The exact constancy of both these quantities cannot however be regarded as proved unless the data are extended down to the freezing point, which it is hoped to do in a further set of experiments.

It is also important to determine accurately the shape of the curve over any one step, which can best be done by averaging the variation observed over a range of about 17°C. in each of the six steps for which data can be obtained from Fig. 5. For this purpose we plot each step starting with the origin at the relevant coordinates of (E′/R)/1000 and temperature given in Table 5, and then obtain the means of the corresponding sets of points for each value of $\Delta T = (T - T_m)$. This process yields the mean values given in Table 6 and plotted in Fig. 6. The flat part of the step is seen to extend over about 4°C., i.e. one-third of the temperature interval between steps, while the oblique portion extends over the remaining two-thirds. Since the size of the measuring intervals is 2.5°C. and the averaging of the six segments obscures some of the detail over another ±1°C., it appears that, even for an infinitely small measuring interval, the flat region of the experimental curve of Fig. 6 will be increased by at most 2°C. on either side. The extent of the horizontal portion is therefore definitely less than 8°C. its most probable value being 6.0 ± 1.0°C. It follows that the extent of the oblique portion is $12.1° - (6.0 \pm 1.0°)$, i.e. $6.1° \pm 1.0$°C. Thus the transition from one step to the next appears to be spread over a range of nearly 6°C., and should therefore be of the second order, like the magnetic (ferromagnetic ⇌ paramagnetic) transformation and the order ⇌ disorder transition in alloys, etc. The energy jump at each step is equal to 0.135×0.086 e.v. = 0.012 e.v., which corresponds to energies in the far infra-red region of molecular rotations. It must

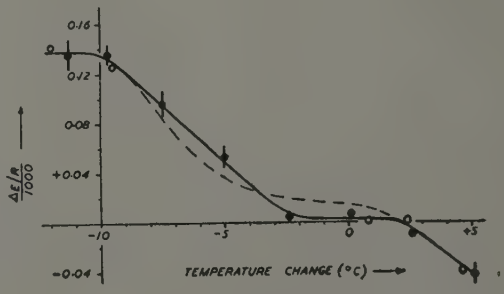

Fig. 6.—The full line shows the mean variation of (E/R)/1000 over one step, the standard errors of the plotted points being indicated by the short vertical lines. The broken line is drawn for a truly sinusoidal variation. The hollow circles have been plotted by shifting the solid circles through 12.0°C. and 0.135 units of (E/R)/1000.

TABLE 6.—AVERAGED VARIATION OF $\frac{\Delta E/R}{1000}$ OVER ONE COMPLETE SEGMENT.

$T = T - T_m$ (°C)	−11.3	−9.7	−7.5	−5.0	−2.4	+0.1	+2.6	+5.1
$\left(\frac{\Delta E/R}{1000}\right)_{corr.}$	0.133 ±0.012	0.134 ±0.008	0.094 ±0.010	0.054 ±0.008	0.005 ±0.004	0.007 ±0.003	−0.009 ±0.002	−0.041 ±0.008

however be noted that the standard deviations of the mean values of Table 6 and Fig. 6 are considerable, amounting to as much as 10% of the value of the energy step, and are about twice what had been expected from the accuracy of the experimental data. This leaves room for the possible presence of some steps or other variation with a smaller temperature interval than 12°C., for the further investigation of which it is desirable to obtain experimentally the complete equation of the transition curves between steps, from more precise measurements using a smaller measuring interval of 1°C. It may, nevertheless, be pointed out that the experimental curve is not sinusoidal, cf. the very significant departure from the sinusoidal curve depicted by the broken line in Fig. 6.

6. The Variation of the Factor A

Finally, it is to be noted that the variation of ln 1/A, where A is the concentration factor in the Andrade equation, $\eta = A \exp\left(\frac{E}{RT}\right)$, (6) runs parallel to that of E/R. This result was noted in previous papers, and can be shown to be generally true, because we have

$$\frac{E}{R} = -T^2 d \ln \eta/dT, \text{ which yields}$$

$$-d \ln\eta = \frac{E}{R}\frac{dT}{T^2},$$

$$\text{i.e} -\left|\ln \eta\right|_1^2 = \int_1^2 \frac{E}{R}\frac{dT}{T^2} = -\left|\frac{E}{RT}\right|_1^2 + \int_1^2 \frac{d}{dT}\left(\frac{E}{R}\right)\frac{dT}{T}$$

after integration by parts, and therefore

$$\left|\frac{E}{RT}\right|_1^2 - \left|\ln\eta\right|_1^2 = \int_1^2 \frac{d(E/R)}{T}. \quad (7)$$

From equation (6) we get $-\ln A = \frac{E}{RT} - \ln \eta$, whence we obtain with the help of equation (7),

$$\Delta \ln (1/A) = -\left|\ln A\right|_1^2 = \left|\frac{E}{RT}\right|_1^2 - \left|\ln \eta\right|_1^2$$

$$= \int_1^2 \frac{d\,(E/R)}{T} = \overline{(1/T)} \int_1^2 d\,(E/R)$$

$$= \overline{1/T}\,\Delta\left(\frac{E}{R}\right), \quad (8)$$

where $\overline{(1/T)}$ is the mean value of 1/T in the range of temperatures considered. This result shows that the variation of ln(1/A) in any small temperature range is $\overline{(1/T)}$ times the corresponding variation to E/R, and indicates that the variations of ln 1/A and those of E/R are both brought about by one and the same characteristic property of the molecules. Equation 8 enables us to estimate $\Delta \ln 1/A$ over any one segment such as in Fig. 6. If we take the mean temperature as 80°C., then T=353°, and $\overline{(1/T)} = 2.83 \times 10^{-3}$, so that Δ (ln 1/A) for one step is equal to $2.83 \times 10^{-3} \times (0.135 \pm 0.009) \times 1000 = 0.382 \pm 0.025$

This makes the ratio A_1/A_2 of the two concentration factors equal to 1.46 ± 0.04, which is definitely not an integer, but may approximate either to 3/2 or to $\sqrt{2}$.

Acknowledgement

The authors are indebted to Dr. Salimuzzaman Siddiqui for his interest in the problem, to Dr. M.R. Choudhry, the then Head of the Chemistry Department, University of Karachi, for allowing the research for the M. Sc. degree to be carried out at the Central Laboratories and to Mr. A.K.M. Ahsanullah for helping with the calibration of the Beckmann thermometer scale.

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EVALUATION OF STORAGE CHARACTERISTICS OF EMULSION TYPE PRINTING INKS

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Introduction

An important problem in the development and manufacture of printing inks is the control of their consistency characteristics, which are fundamental factors in determining its suitability for printing. The evaluation of rheological properties affords an excellent means of following changes of consistency on storage, and the present paper deals with a study of these characteristics for the emulsion inks developed at the Central Laboratories. The behaviour of the ink after a short period of high-speed stirring has also been investigated to study the possibilities of using this test for the indication of its storage characteristics thereby obviating the necessity of prolonged tests. This method has previously been investigated by R.J. Woodbridge[1] for some types of emulsion paints.

The predominant rheological characteristic of most oil-based inks is thixotropy, and the addition of water to such an ink may lead to (a) straight emulsification of water in the organic vehicle and (b) flocculation of the pigment particles. These two phenomenon may occur separately or together, depending primarily upon the pigment to vehicle wetting relations of the system. Emulsions may therefore show far more thixotropy than oil-based inks.

Experimental Details

The ink was prepared by adding a water solution of emulsifying agent to carbon black dispersed in hydrocarbon oil with the aid of a suitable dispersing agent. In the present study consistency measurements have been made on eight formulations which are given in Table 1, and have been chosen in order to study the effect of:

TABLE 1.—DETAILS OF FORMULATIONS.

No.	Pigment %	Vehicle %	Dispersing agent %	Water containing emulsifying agent %
1	6.0	49.0	0.0	45.0
2	6.0	44.0	5.0	45.0
3	6.0	39.0	10.0	45.0
4	6.0	34.0	15.0	45.0
5	6.0	41.5	7.5	45.0
6	6.0	39.0	7.5	47.0
7	6.0	36.5	7.5	50.0
8	Imported sample containing 42% water.			

*Corresponds to adopted C.I.S.R. formulation.

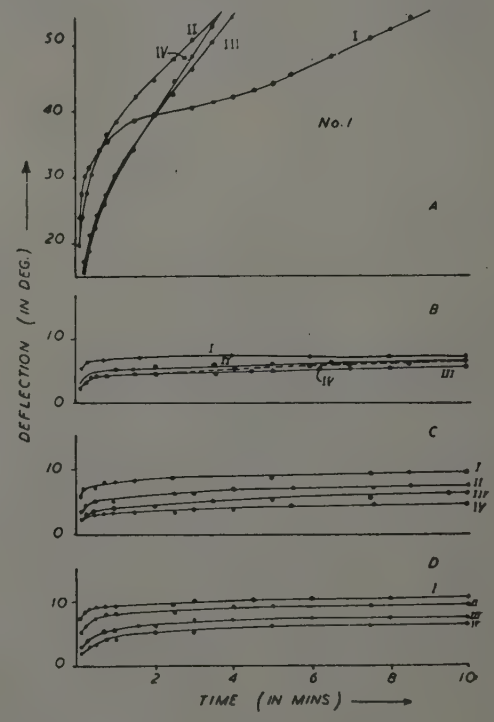

Fig. 1

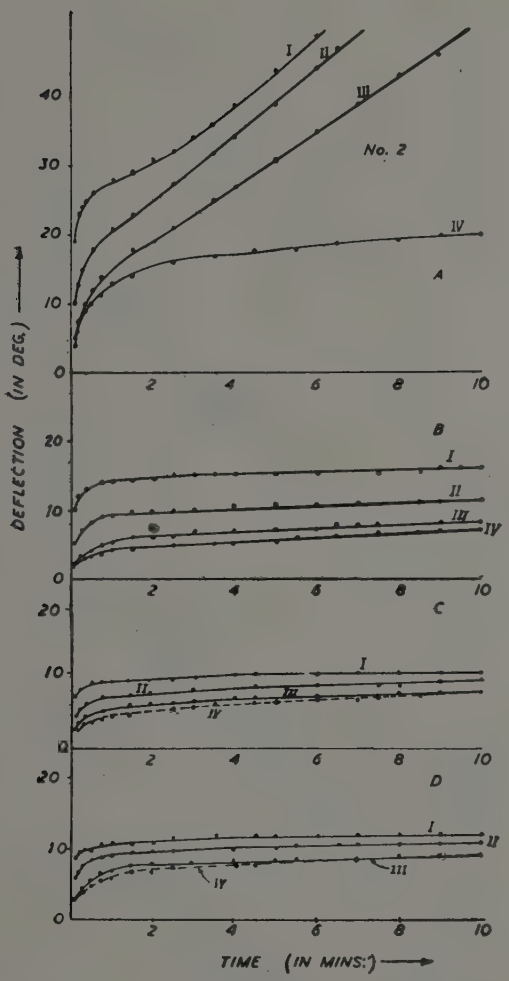

Fig. 2

(i) variation of wetting characteristics between pigment and vehicle by changing the proportion of dispersing agent, and

(ii) variation in the quantity of water, while keeping the quantity of dispersing agent constant.

A measure of thixotropy of the ink, which is in the form of a paste, was obtained by means of a Gallenkamp torsion-wire viscometer. The cylinderical bob (diameter 1⅝") susp nded from the torsion wire (30 SWG) was immersed in the material under test, the sample was stirred

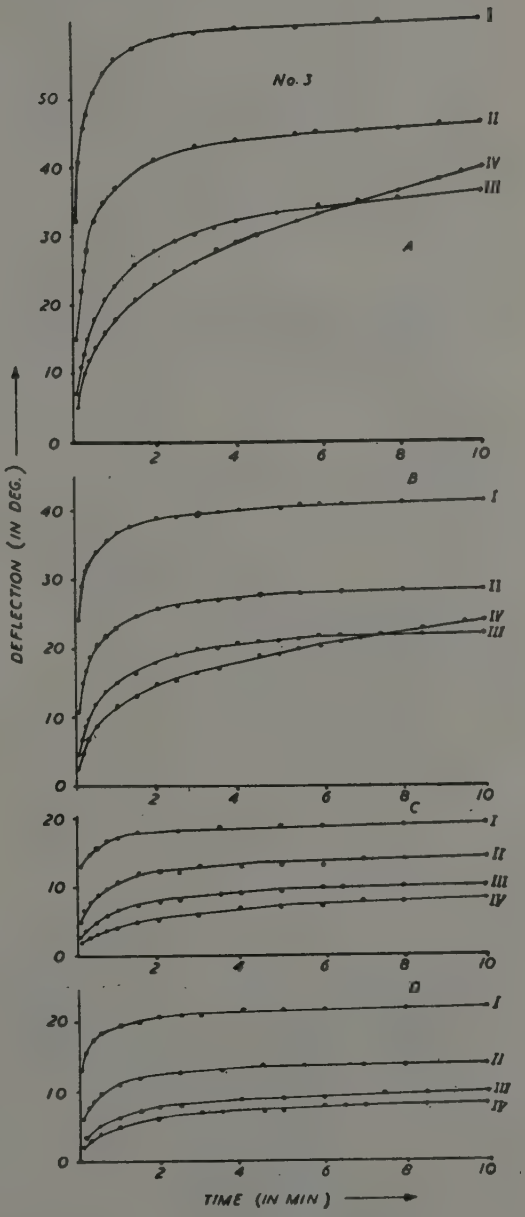

Fig. 3

and after a certain time, the head of the wire was rapidly rotated through 180°C. The rotation of the bob was noted and plotted in term of angular deflection against time. The test was repeated

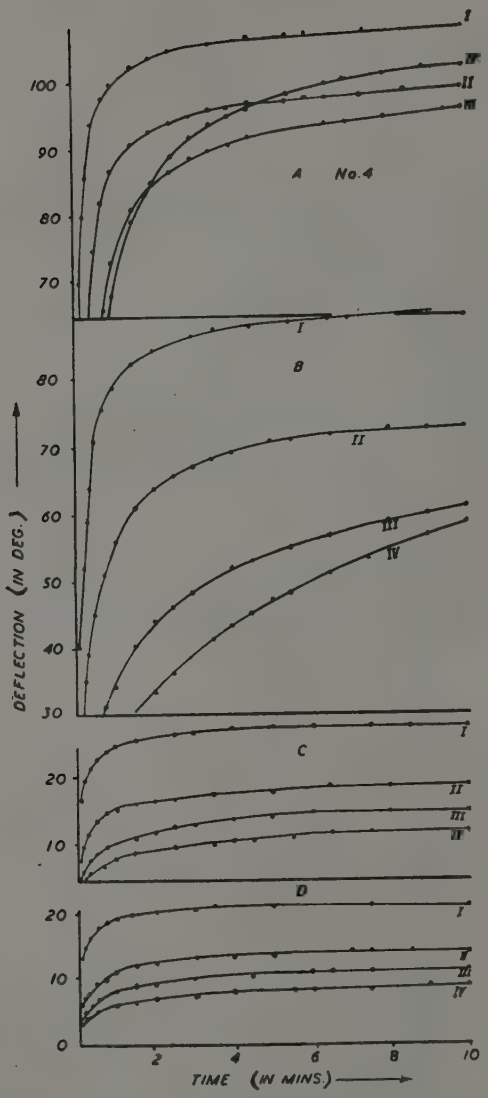
A No.4
B
C
D
DEFLECTION (IN DEG.)
TIME (IN MINS.)

Fig. 4

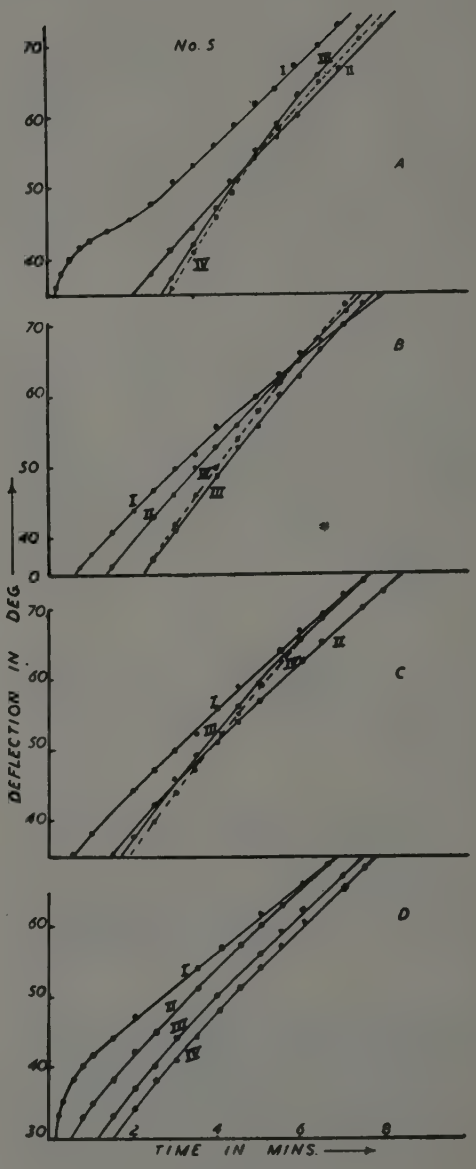
No. 5
A
B
C
D
DEFLECTION IN DEG.
TIME IN MINS.

Fig. 5

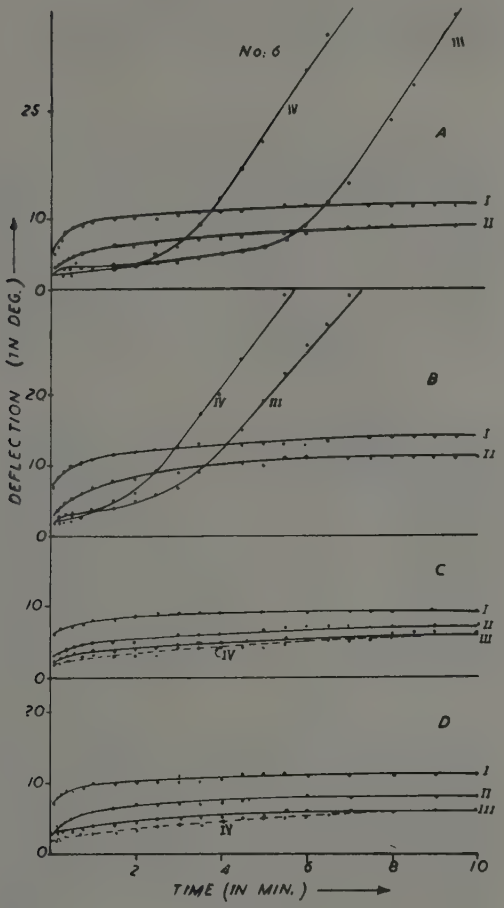

Fig. 6

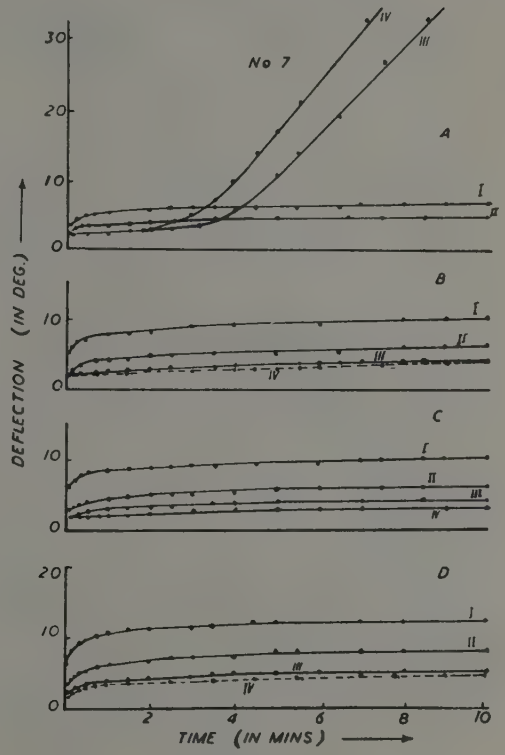

Fig. 7

TABLE 2.—RESULTS OF RHEOLOGICAL MEASUREMENTS.

No.	(A) As made	(B) After high-speed stirring for one hour	(D)* After incubation for 4 days at 40°C.
1	Undefined behaviour	Great increase in viscosity	Same as in test (B)
2	Thixotropic	Increase in viscosity	Greater increase in viscosity than in test (B)
3	,,	Slight increase in viscosity	,,
4	,,	Increase in viscosity	Much greater increase in viscosity than in test (B)
5	Non-thixotropic	Virtually no change	Virtually no change
6	Abnormal behaviour	,,	No change in viscosity. Abnormal behaviour disappears
7	,,	Slight decrease in viscosity. Abnormal behaviour persists	Greater decrease in viscosity than test (A). No abnormal behaviour
8	Non-thixotropic	Virtually no change	Virtually no change

*The results for (C) do not differ significantly from those for (D), and are therefore not given separately.

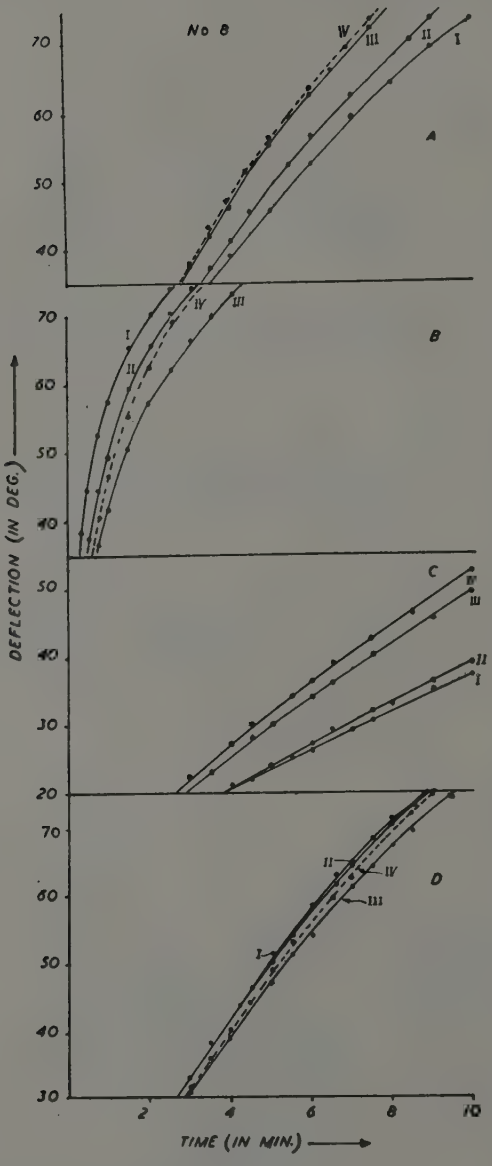

Fig. 8

with varying periods of rest, from 0 to 5 minutes. Typical graphs obtained for the series of eight formulations are shown in Figs. 1 to 8.

Results

Generally speaking, the greater the difference between the extreme graphs (i.e. no rest and 5 minutes rest after stirring), the greater is the thixotropy of the system and therefore these graphs provide comparative data for testing, which are useful in assesssing changes on storage. In the present work, each formulation was tested under four different conditions: (A) when the ink is freshly made, (B) after one hour high-speed stirring, (C) afte further 4 days standing, and (D) after 4 days incubation at 40°C.

The results of the rheological measurements for A,B and D are given in Table 2, those for C being omitted because they do not differ significantly from D. It is seen from the table that the results of tests B and D are essentially similar, except that the formulations 6 and 7, where the proportion of water is increased nearly to saturation point, behave abnormally when freshly made and in test B. In practical user's tests it has been found that formulations Nos. 3 and 5 are satisfactory for printing purposes, even after 18 months storage.

It therefore appears that high speed stirring of a sample under test gives a rapid indication of changes that might take place on storage, and if an unknown sample fails to pass this high speed test then the other tests may be dispensed with. If however it appears quite stable after high speed stirring, then it is desirable to carry out incubation tests, because some formulations (e.g. No. 4) show only slight increase in viscosity after high speed stirring test but significant increase after the incubation test.

Acknowledgements

The authors are grateful to Dr. M M. Qurashi for his continued interest in the problem and to Mr. S. Malik for help with some of the experimental work.

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SPECTROPHOTOMETRIC STUDIES ON TRANSITION COMPLEXES IN CIS-TRANS INTERCONVERSION

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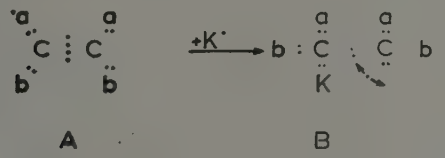
It is well known that only paramagnetic substances catalyze the *cis-trans* interconversion, for which the following mechanism has been adopted generally:



A B

Accordingly, it can be expected that all oxides of nitrogen (except nitrous oxide) and oxygen, which have one feature in common, namely an odd number of electrons giving rise to three-electron bonds,[1] as shown in Fig. 1, will catalyze this *cis-trans* conversion. It has been proposed previously by the author[11,12] that the oxygen molecule may interact with electrons through hydrogen bonding with the formation of a six-membered transition ring. Under such circumstances, the pull of π electrons and their subsequent recovery cause *cis* to *trans* conversion, but the complexing oxygen once changed from its inert structure[12,19] seems to be highly reactive in getting attached to the carbon chain and shifting the newly generated *trans* double bond to adjacent position. In both nitrogen dioxide and oxygen conversion of *cis* to *trans* form through transition complexes, (as shown at B above), the transitory removal of electrons in a *cis* double bond leaves a single bond structure for easy change over to *trans* form. This common aspect of the *cis-trans* interconversion has been investigated and confirmed through various experiments, described in the present paper.

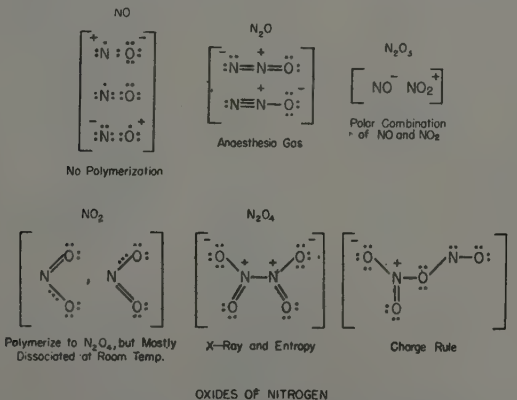


Fig. 1.—Oxides of nitrogen and probable structures.

All nitrogen oxides were not found to be isomerizing agents. Nitrous oxide did not form any nitrogen derivative with oleic acid, nor did it convert *cis* form to *trans* form. Figure 3 shows the infrared absorption at two regions by the different reaction products from vessel I-III of Fig. 2. Nitrogen derivatives (6.10μ and 6.44 μ) were formed in large quantities by all sets of the reactions. However, the amount of *trans* isomer (10.32 μ) produced was highest in the case of nitrogen dioxide reactions (III), smaller with the total oxides of nitrogen (I) and none in the case of nitric oxide reactions (II). Moreover, while the reactions were going on, the temperature of the substances in vessels I and III rose to over 80°C. but there was no temperature rise in the reaction vessel II. Such processes of bubbling nitrogen dioxide, when applied to linoleic and linolenic acids, caused instantaneous polymerization.

Dinitrogen trioxide reactions produced

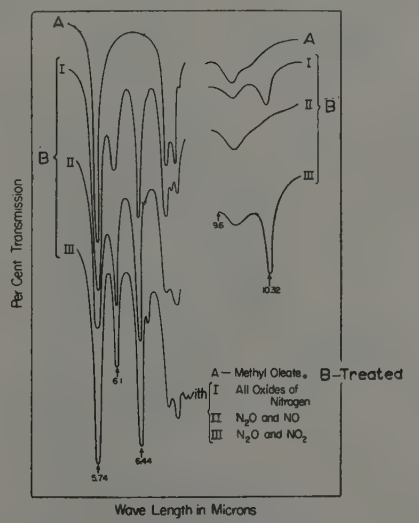


Fig. 3.—Infrared analysis on isomerization products of methyl oleate.

considerable amounts of nitrogen derivatives with a minimal conversion of *cis* configuration to *trans*. Nitric oxide and dinitrogen trioxide appeared to be the additive reagents; the minor conversion of *cis* to *trans* form by dinitrogen trioxide might have resulted from some possible contamination of dinitrogen trioxide by free nitrogen dioxide.

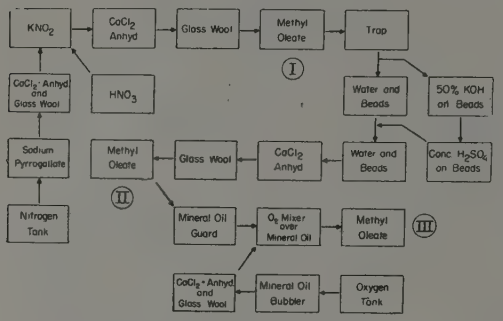


Fig. 2(a).—A scheme for isomerization reaction.

Formation of Labile Species of Products

The foregoing rapid reactions by nitrogen dioxide did not reveal all aspects of fatty acid behaviour. The slow processes of nitrogen dioxide reactions were then arranged by a gaseous atmosphere of nitrogen dioxide in a desiccator that contained fatty acid in thin layers. In the presence of nitrogen dioxide, methyl linoleate gave a definite absorption in the ultraviolet region at 249 mμ (Fig. 4), which increased gradually to maximum intensity after 4 hours and then decreased until it disappeared after 8 hours. Methyl linolenate showed absorption at 310 mμ (Fig. 4) after 10 minutes which reached its

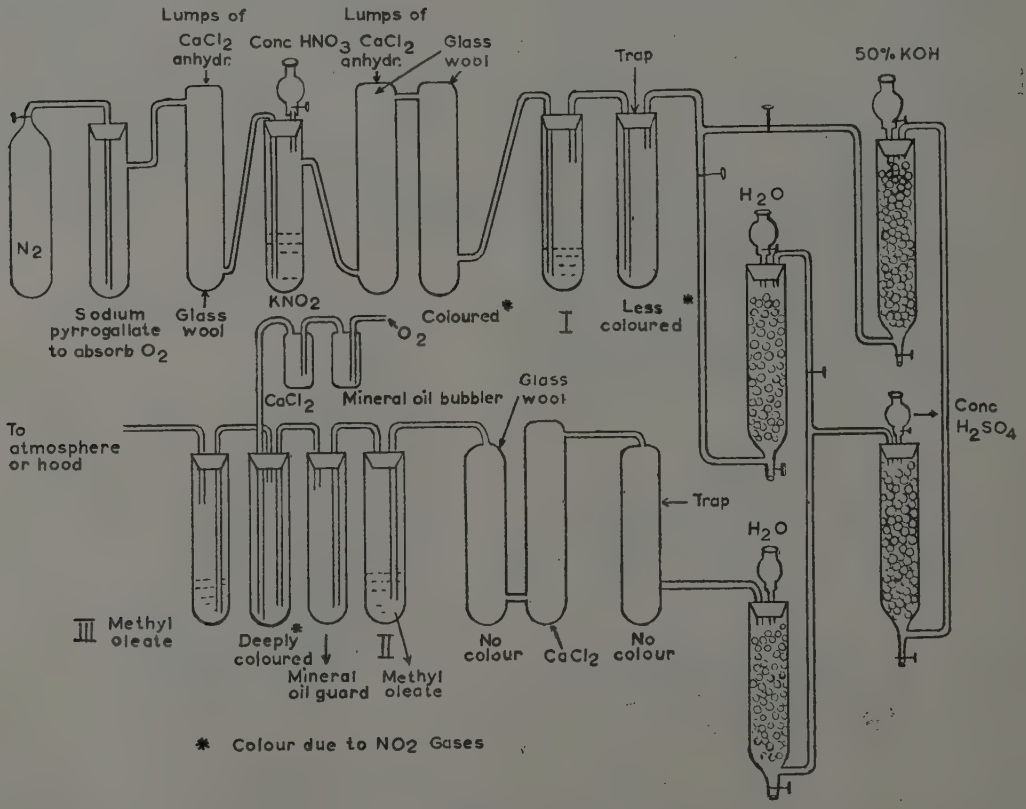


Fig. 2(b).—Reaction sytems.

maximum after 30 minutes. Another interesting phenomenon in methyl linolenate isomerization reactions was that it yielded some labile *trans* isomer (absorbing at 10.32 μ) that disappeared under vacuum. A portion of methyl linolenate, after reaction with nitrogen dioxide for 15 minutes, was subjected to infrared analysis to obtain the solid line curves (A & B, Fig. 5), and another evacuated portion gave rise to the dotted line curves (A′ & B′, Fig. 5). These curves show two important regions, 3.5-7.1 μ (nitrogen derivative absorbing at 6.42 μ) and 9.6-10.8 μ (*trans* isomer at 10.32 μ); methyl linolenate does not have any band at 6.42, nor any at 10.32 The application of vacuum increased the amount of nitrogen derivatives (6.42 μ, curve A′) and eliminated almost all of the *trans* forms (curve B′, 10.32μ).

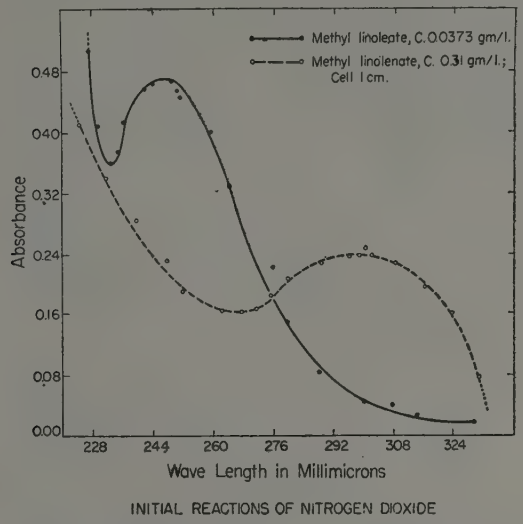


Fig. 4.—Ultraviolet absorption curves of methyl linoleate and linolenate reacting with NO_2.

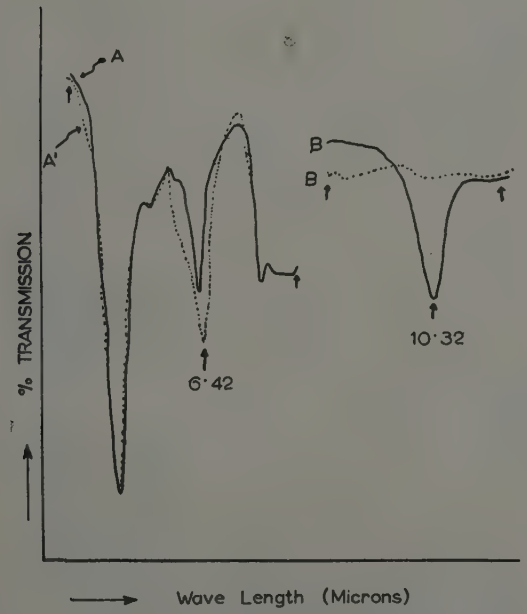


Fig. 5.—Infrared spectra of labile trans isomer of methyl linolenate before (A and B) and after (A′ and B′) evacuation.

Combined absorption studies at 301 mμ in the ultraviolet region and 10.32 μ in the infrared region during the reactions of nitrogen dioxide with methyl linolenate showed that as long as the absorption at 301 mμ persisted, *trans* isomer (10.32 μ) was not observed (Figs. 6 and 7) but

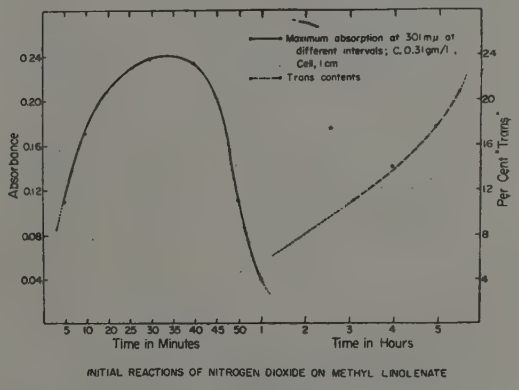


Fig. 6.—Transition complex and trans isomer during the reactions of NO_2.

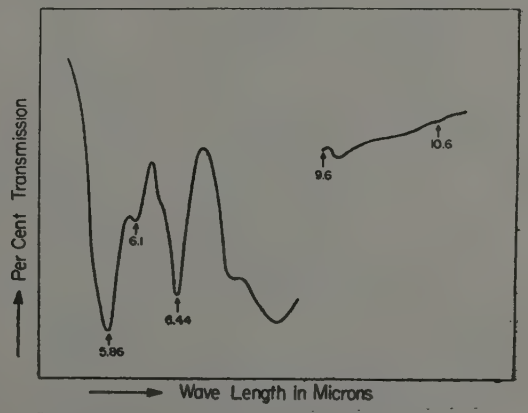


Fig. 7.—Infrared adsorption bands for nitrogen derivatives.

nitrogen derivatives were formed (6.44 μ). Methyl linoleate exhibited the same phenomena with its analogous absorption at 249 mμ during the reactions with nitrogen dioxide. Under similar conditions, methyl oleate did not absorb in the ultraviolet region investigated, and the *trans* isomer was found to be formed from methyl oleate, but only aftter 8-hour exposure to the atmosphere of nitrogen dioxide giving initially a blue transient colouration[25] indicating an unstable complex. Hence, one or more unstable species appeared to be formed prior to *cis-trans* conversion. These probably resulted in unstable complexes, which gave rise to either *trans* isomer free of nitrogen derivatives or stable nitrogen derivatives found in the experiments. Each fatty acid ester thus required certain periods of time to initiate *cis* to *trans* conversion by nitrogen dioxide: methyl oleate, 8 hours; methyl linoleate 1/4 hour; and methyl linolenate, 1/6 hour.

In the same way, oxygen conversion of *cis* to *trans* form indicated such definite and characteristic induction periods: methyl oleate, 45 days; methyl linoleate, 16 hours; and linolenate, 4 hours only (all at room temperatures). Oxygen reactivity is thus lower than nitrogen dioxide but both have possibly similar mode of reactions during the induction periods, i.e. complex formation involving a pull on π elctrons, as previously noted.

Table 1 gives the picture of *trans* conversion in different types of isomerization of *cis* form by nitrogen dioxide, as well as by oxygen. The different conditions, temperature and gaseous states in particular, play predominant roles in *cis-trans*

TABLE 1.—FORMATION OF TRANS ISOMERS.

No.	Isomerizing agents	Substances isomerized	Temperature 0°C.	Other conditions	*Trans* conversion in reacting molecules %	Additional remarks
1	Nitrogen dioxide	Methyl oleate	28-30	Bubbling gases	46	Some polymerization[a]
2	,,	,,	,,	Atmosphere of gases	57	,,
3	,,	,,	,,	Mixture of solid KNO_2 + conc. HNO_3 + oleate +agitation by air	51	,,
4	,,	Oleic acid	,,	,,	54	,,
5	,,	Methyl linoleate	,, ,,	Atmosphere of gases	21	Heavy polymerization[a]
6	,,	Methyl linolenate	,,	,,	14	,,
7	Oxygen molecules	Methyl oleate	,,	Agitation by air	66	No polymerization
S	,,	,,	45	,,	77	Some polymerization[b]
9	,,	Methyl linoleate	−10	,,	88	No polymerization
10	,,	,,	0	Still atmosphere in cooler	90	,,
11	,,	,,	28-30	Agitation by air	54	Heavy polymerization[b]
12	,,	Methyl linolenate	−10	,,	87	No polymerization
13	,,	,,	28-30	,,	44	Heavy polymerization[b]
14	,,	,,	−10	Still atmosphere in cooler	90	No polymerization

[a]Polymers as nitrogen derivatives. [b]Polymers as oxygenated compound.

isomerization. The conversions in both types are systematic and start after definite induction periods and consequently quite similar in nature. The slow rate of oxygen favours conversion to *trans* rather than that to polymers. The faster rate of nitrogen dioxide facilitates the reverse processes and consequently *trans* contents are lower in 1-6 items (Table 1). Furthermore, cooler temperature still cuts down the reactivity of oxygen and causes better conversion to *trans* (cf. items, 9, 10, 12 and 14 in Table 1).In the same way, lower reactivity of nitrogen dioxide in gaseous atmosphere (cf. previous desiccator reactions and items 2 and 4 of Table 1) increases the yield of *trans* isomer.

Ultimate Products of Isomerization

There is another phase of *cis-trans* interconversion, in which the recovery of π electrons is not possible, and either the simple or polymeric derivatives are formed. Both nitrogen dioxide and oxygen yield polymeric derivatives with the advance of reactions, nitrogen dioxide (being a stronger reagent) producing a greater degree of polymerization than oxygen which produces no polymer at the start. Furthermore, long-term reactions of nitrogen dioxide and oxygen with methyl oleate, linoleate and linolenate resulted in complete polymerization. This has been shown through urea complex formation, petroleum ether treatment and time-isomerization, discussed below.

The nitrogen dioxide polymers showed identical nitrogen analysis through Dumas and Kjeldahl methods: oleate polymers, 4.5%; linoleate polymers, 5.1%; and linolenate polymers, 5.9% nitrogen. These correspond to one N-atom (i.e. one NO_2) per fatty acid chain, indicating addition reactions.

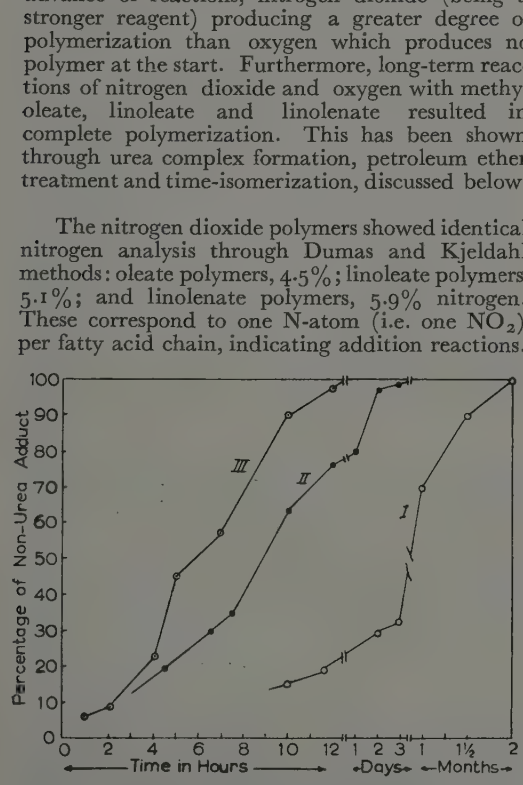


Fig. 8.—Formation of non-urea adducts during the reaction of NO_2 with : I, methyl oleate ; II, methyl linoleate; and III, methyl linolenate.

Hence *cis-trans* interconversions may be taken as the processes preceding the addition reactions, substantiating the mechanism in this paper and concepts proposed by Marvel.[10] Such polymer formations with one O_2 per chain have been formulated by various investigators.[30]

Since urea forms complexes with monomers and not with polymers, nitrogen dioxide isomerization products have been systematically analyzed through urea complexes. The nitrogen derivatives were found to be mostly polymers as non-urea adducts (Fig. 8), while the urea adducts (complexes) were almost free from nitrogen. Such urea complex formation conducted for each batch of reaction products established the trends of polymer formation (Fig. 8), the degree of which in relation to nitrogen derviatives and *trans* isomers was also measured. Under the conditions of isomerization, the periods of time manifesting the peak formation of *trans* isomer were noted as follows: 14-20 hours for oleate ; 7½-9 hours for linoleate, and 2-3 hours for linolenate. With longer periods of isomerization, the *trans* isomer in each case was found to disappear entirely (methyl oleate, 1½ months; linoleate, 27 hours; linolenate, 8 hours). Similar trends of reactions are also followed by oxygen isomerization. Some authors [31] have investigated *trans* - and polymer-formation by oxygen on different fatty substances. Since the reactions are slow, the systematic studies could not be arranged in the present investigation, but in our open shelf experiments (without much attention) complete polymerization occurred in approximately 2¼ years for methyl oleate, 7 months for the linoleate and 2½ months for the linolenate. *Trans* conversion is caused [11,32,33] by oxygen upto a maximum limit, as with nitrogen dioxide noted above and then *trans* isomer also disappears entirely, yielding only polymers.

During the processes of the determinations of polymers, it was noted in the case of oleic acid isomerized by nitrogen dioxide that, when elaidic and unisomerized oleic acid were obtained as urea complex crystals, elaidic acid always precipitated out first (as urea complexes) and oleic acid after a considerable time lag. This preferential urea complex formation by elaidic acid over oleic acid probably relates to their physical structures. Figure 9 shows schematically the structures of elaidic and oleic in plane projection of the skeleton C-chain. *cis*-Oleic is seen to be folded, which makes it difficult for oleic acid molecule to slide into the hexagonal urea cylinder,[9] whereas the straight chain character of elaidic acid offers easy access to the same. The easy urea complex formation by stearolic acid[34] as against *cis*-oleic acid also confirms these ideas on

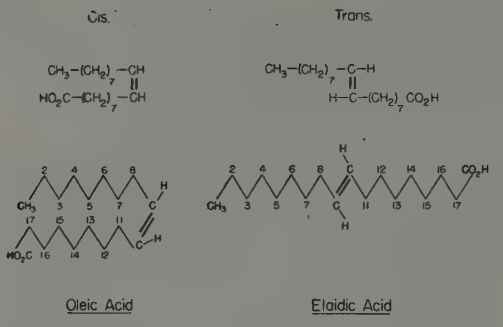


Fig. 9.—Probable projection C-skeleton of oleic and elaidic acids.

straight chain structure. (The triple bond between two carbon atoms eliminates the possiblity of folded nature). In the oxygen reactions, the *trans* hydroperoxides gets concentrated first through urea complexes from *cis* isomers. Here also, oxygen like nitrogen dixoide helps *trans* conversion with accompanying straight C-chain from the *cis* folded structure.

Detailed Mechanism of Interconversions

From the comparative picture of the nitrogen dioxide and oxygen reactions, presented above, it is evident that *cis-trans* interconversions by both these agents follow almost similar processes pointing to the common pathways of mechanisms. Although complex formation has already been proposed for oxygen [11-12] reactions, the details of *cis-trans* interconversion in fatty materials by nitrogen dioxide and oxygen have not been fully settled. The other isomerizing agents causing *cis-trans* interconversion, such as, sulphurous acid or a saturated solution of sodium bisulphate, phosphorous acid, sulphur, selenium, nitrous acid, and milder reagent, iodine, are more or less known as complex-forming or initiating loose complexes in completing an electronic closed configuration. [35-42] The labile π electrons of the *cis* double bond facilitates formation of such a circuit.[41]

The behaviour of nitrogen dioxide indicates the formation of a series of complexes, during the isomerization reactions. Hence, the reaction mechanisms of nitrogen dioxide may be depicted as follows: The initial reactions may lead to a molecular complex (I, Fig. 10), which passes through a transition state of labile *trans* configuration (shown with wavy bonds) and transient C-C single bond (II) that helps free rotation and formations of the intermediate *trans* form (III). That the *trans* form complexes as such may be labile, is shown by the processes of vacuum

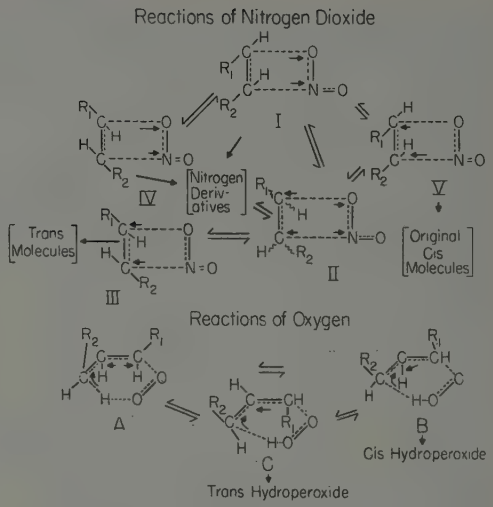


Fig. 10.—Mechanisms of cis-trans interconversion by NO_2 and O_2.

causing disappearance of *trans* isomer (Fig. 5) during the reactions of methyl linolenate. Its disappearance on release of nitrogen dioxide pressure under vacuum, indicates the association of nitrogen dioxide by non-ionic molecular forces [20,44-46] due to π electrons. Most probably, the hydrogen atoms in -C=C- double bond gain enough freedom from the influences of π electrons and vibrate around transient C-C single bond so formed for absorption at 10.32μ. The recovery of π electrons by such C-C bond may release nitrogen dioxide and form stable *trans* molecules of fatty acid esters. However, sharing of π electrons by nitrogen dioxide may yield nitrogen derivatives through molecular complexes (I, IV). *Cis* molecules may also result through complexes (V). The three types of products, *cis* and *trans* isomers of oleate and linoleate, and polymers have been isolated (by chromatographic analysis) and will be discussed in a separate communication.[29]

Cis-trans interconversion in reactions by oxygen is similar to that by nitrogen dioxide, but appears to involve hydroperoxidations, which drew attention of general workers [13-15] and especially in autoxidation of unsaturated fatty acid esters.[11,12,21] The variations in the environmental conditions influence these isomerizing reactions by oxygen molecule[19] to a considerable extent (Table 1). These processes prevail in the earlier stage of autoxidation, which has always been neglected by the kineticist [13,14,15] because of the fact that it does not appreciably contribute to the main autoxidation reactions.[16-18,30-31]

Experimental

Preparation of Different Materials.—The low-grade samples of the acids (oleic (95-97%), linoleic (85-90%), and linolenic (80-85%)) and their methyl esters were obtained by fractionation of cottonseed and linseed oil acids and esters through urea complex formations.[2] The pure methyl oleate (I. N. = iodine number, 86.2) was prepared by the method of Khan.[3] Methyl linoleate (I.N., 172.4) and linolenate (I.N., 259.6) were prepared by the usual bromination and debromination procedures.[4]

Nitric oxide was prepared by the second method described by Farkas and Melville.[5] Nitrogen dioxide was obtained by mixing pure nitric oxide with oxygen.

Determination of Unsaturation and the Contents of Nitrogen and Polymer.—The iodine number was determined by the Wijs' half-an-hour method. The quantitative determination of nitrogen was made by micro Kjeldahl[26] and Dumas' methods.[27] The polymer formation was estimated by: (a) insolubility of the products in petroleum ether, b.p. 30-60°C. and free from the unsaturates;[6] (b) the products not forming urea complexes.[7,9] For (a), the crude reaction mixtures were shaken with any amount of petroleum ether, as many times as possible to remove the soluble materials completely. The residue was noted as polymer, as the monomers used were soluble in petroleum ether. In the second case, Swern, Schlenk and Holman have put forward the usually employed "solution method" for urea complex formation. The only important thing to be noted was to remove all materials forming urea crystals by using any amount of methyl alcohol or urea, as necessary. The filtrate contains non-urea complex substances that can be easily measured.

Spectrophotometric Analyses.—The degrees of *cis-trans* interconversion and of formation of the nitrogen derivatives in all materials and in the reaction products were determined by comparative studies of infrared absorption by the Perkin Elmer Instrument, Model 21. The base line technique in conjunction with the absorption of pure elaidic acid and methyl elaidate were used to determine the percentage of *trans* contents.[22,23] The tested wave lengths were 9.0-12.0μ (particularly, 10.32μ) for the isolated *trans* double bond and 5.0-7.5μ for the nitrogen derivatives. Swern and Wheeler[22] have dealt with these analytical methods in enough details.

The Beckman DU model spectrophotometer was employed for the ultraviolet absorption analysis. The procedures involve common experiments using absolute alcohol (distilled over zinc powder and potassium hydroxide pellets) as 1% solution with the substances for analysis in the range, 222 mμ to 350 mμ recording diverse aspects of interest[24] in fat chemistry. Multiple dilution method was employed, if the density of absorption is very intense.

Reactions of Nitrogen Oxides on Oleic Acid and Methyl Oleate.—Fifty grams of oleic acid (95-97%) was treated with nitrous oxide for several days without any isomerization (analysis: nitrogen, 0.0; *trans*, 0.0). The train of gas reaction was set up as in the flow sheet shown in Fig. 2 and reaction systems in Fig. 2(a), to study individually the effects of other nitrogen oxides. All nitrogen oxides, generated (N_2O, NO, NO_2, N_2O_3, etc.) by nitric acid and nitrite, were allowed to react with 50 g. of crude methyl oleate (reaction vessel, I). After nitrogen dioxide and dinitrogen trioxide were washed off by (a) water or by (b) 50% potassium hydroxide, concentrated suphuric acid and water, the remaining nitrogen dioxide and nitric oxide were dried by anhydrous calcium chloride and caused to react with another 50 g. of methyl oleate (reaction vessel II). The oxygen was mixed through a proper device with the out-going gases changing the nitric oxide to nitrogen dioxide. Thus, nitrous oxide and nitrogen dioxide passed through the third sample containing 50 g. of methyl oleate (reaction vessel III). Since nitrous oxide was inactive, the degrees of isomerization and addition reactions by all nitrogen oxides in vessel I, by nitric oxide in vessel II, and by nitrogen dioxide in III, were determined by chemical and physical analyses (Fig. 3). The flow-sheet description (Fig. 2) should help workers using their own devices and other details and make the materials clear at a glance. The processes of washing by potassium hydroxide and sulphuric acid assured the absence of nitrogen dioxide and dinitrogen trioxide according to the previous workers. The reactions of methyl oleate, by all oxides of nitrogen (vessel I, analysis *trans*, 31.0%; polymers, 27.0% containing 4.9% nitrogen; *cis* unchanged oleate, 36.0% and unaccounted, 6.0%), by nitric oxide only (vessel II, analysis: *trans*, 0.0; polymer, 54.0%; *cis* unchanged oleate, 38.0%; unaccounted, 8.0%), by nitrogen dioxide (vessel III, analysis: *trans* 33.0% polymer, 34.0% containing 5.3% nitrogen; *cis* unchanged oleate, 29.0%; unaccounted, 4.0%), were, thus, performed.

Dinitrogen Trioxide.—In the case of dinitrogen trioxide reactions, equivalent amounts of nitric oxide and nitrogen dioxide were mixed in a tube containing glass wool. This tube was slightly warmed[8] by a heating coil. The effluent gas was

allowed to pass through a coil immersed in chipped ice and was then allowed to bubble through pure methyl oleate (10 g., I.N., 84.8) in a closed test tube, precooled to 0°-3° C. by chipped ice plus salt. Both the reaction systems were freed of oxygen at the beginning and of nitrogen oxides at the end of the reactions by flushing with oxygen-free nitrogen gas. The analysis of reacted oleate gave: *trans*, 4.0%; polymer, 61.0% containing 5.1% nitrogen; unchanged, 29.0%; and unaccounted, 6.0%.

Reactions of Nitrogen Dioxide on Linoleic and Linolenic Acids.—The nitrogen dioxide gas was bubbled through linoleic and linolenic acids (30. g. each) in tubes for only 15 minutes, until thick polymers (100.0%) were obtained. Analysis of both samples gave: *trans*, 0.0; unchanged monomer, 0.0 soluble in petroleum ether, or giving urea complexes.

Milder Processes of Nitrogen Dioxide Reactions on Methyl Ester of Linoleic and Linolenic Acids.—The bubbling processes of isomerizations, so far employed in the investigations, were drastic and the reactions (those of linolenate in particular) could not be controlled properly. An attempt was then made to use milder conditions. Furthermore, nitrogen dioxide gas being the only effective isomerizing agent, was used in all the other subsequent experiments. Thin layers (1.0-2.0 mm. thickness) of methyl linoleate (10.0 g.) or of linolenate (10.0 g.) in a crystallizing dish was placed inside a dessicator that was filled with nitrogen dioxide. The course of reaction was followed by infrared and ultraviolet absorption analysis at 5, 10, 15 and 30 minutes, and a 1, 2, 4, 6, and 10 hours after the onset of reactions. The absorption maxima were detected at 249 mμ for linoleate and at 301 mμ for linolenate due to some labile transition complexes that disappeared with time (Fig. 4). Even the indication of labile *trans* isomer in the linolenate reactions led to the following experiments.

Preparation of Labile Trans Isomer.—Methyl linolenate (50 g.) was kept in the atmosphere of nitrogen dioxide for 20 minutes. One portion of the sample was subjected to high vacuum. Both the nitrogen dioxide and the vacuum treated samples were subjected to infrared absorption analyses (Fig. 5) in the ranges 5.0-7.0 μ and 9.0-11.0 μ. The absorptions due to nitrogen and *trans* isomer were carefully noted. Methyl linolenate used were analyzed (absorption at 6.42 μ, 0.0; N_2, 0.0; *trans*, 0.0). Nitrogen dioxide treated methyl linolenate after being subjected to vacuum showed characteristics (absorption at 6.42 μ, still stronger band; N_2, 5.9%, *trans*, 0.0).

Detection of Transition Complex and Formation of Trans Isomer.—The above experiments aroused our interest in following variations with time in the amounts of absorption at both 301 mμ in the ultraviolet region and 10.32μ in the infrared region during the reactions of methyl linolenate with nitrogen dioxide. The nitrogen dioxide reactions on linolenate were checked from the very onset for absorption at 301 mμ and 10.32 μ, The suitable intervals for the readings were chosen so as to indicate initiation, maximum formation and disappearance of the transition complexes and *trans* isomer. Figures 6 and 7 show the results.

Detection of Polymers through Urea Complex Formation.—The different fatty materials (50 g. each) reacting were exhaustively freed of the urea complex forming substances through solution method of urea complex formation.[2,43] The polymers were measured from the final filtrate, as they do not form urea complexes. Figure 8 records the trends of polymer formation.

Trans Isomers and Urea Complex Formation.—The solution method[2,43] was again followed with 50 g. of each material. The *trans* isomers were always isolated ahead of the *cis* isomers. Elaidic acid got precipitated faster than oleic acid. Figure 9 establishes the differences of the acids. Table 1 indicates the degree of *trans* isomer formation.

Oxygen Reactions on Fatty Acid Esters.—Methyl oleate, linoleate and linolenate were oxidized by bubbling oxygen gas at room temperatures (28-30°C.). Due to the slow rate of reactions, oxidation took 6 months for oleate, 16 days for linoleate and 5 days for linolenate in order to attain the desired degree of oxidation and *trans* conversion. The samples from each substance were analyzed for *trans* and peroxide contents[28,22] at suitable intervals. Autoxidation was continued until peroxide contents reached 10% level (ca., 625 - 700 m.e./Kg. of peroxide value in these instances). The peroxide formation and appearance of *trans* isomers were almost co-incident as far as time is concerned in all the above substances. Such infrared absorption studies together with ultraviolet analyses at different intervals could not establish the presence of any unstable intermediates formed during autoxidation between oxygen and these fatty substances. The other autoxidation reactions were carried out with the different substances as: (a) methyl oleate at 45 °C., (b) linoleate at 0°C. and linolenate at - 10°C. in the open Erlenmeyer flasks in the coolers without any agitation. The substances autoxidized to the level of 10% peroxides gave analysis for *trans*

contents (methyl oleate, in the range, 6.0-7.0%; methyl linoleate, in the range, 8.5-9.0%; methyl linolenate, in the range, 7.0-8.0%). The oxygenated products were isolated by the following experiments.

Isolation of Trans Isomers from Oxygen Reaction Products.—Since the slowness in oxygen reactions causes loss of time, the reaction products were isolated from the partially oxidized substances (cf. 10%, foregoing section) by countercurrent extraction, according to the methods already described,[12] between pairs of solvents (89% alcohol and petroleum ether, 30-60°C. b.p.). The peroxide concentrates thus quantitatively isolated from different sources almost equal to 10% of the original material taken, were subjected to infrared analyses for determining the contents of *trans* isomer in each sample. The *trans* isomers were usually found to be formed without any side reactions in oxygen processes at the initial stages. Table 1 shows the results.

Oxygen Reactions and Time Effects.—The samples of methyl oleate, linoleate and linolenate were left open to air at room temperatures for occasional analyses of *trans* isomer and polymer contents. Solution method of urea complex formation[2,43] was used for the purpose. *Trans* contents disappeared with total conversion to polymers in time (methyl oleate 2½ years; linoleate, 7 months; linolenate, 2½ months).

Acknowledgement

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STUDIES ON CENTAUREA BEHEN LINN. (COMPOSITAE). PART I

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According to Pharmacographia Indica, Vol. II, p. 303, *Centaurea behen* grows in Iran, Syria and Armenia in two varieties, the white and the red bahman, the roots of which were used as drugs by the ancient Persians. It is mentioned further that the white bahman is free from alkaloids, while the red one contains a bitter tasting alkaloid named bahamine showing an opal blue fluorescence in ether solution from which it crystallises in feathery crystals. Neither the melting point nor analysis or any other data is given.

In Nadkarnis' Indian Materia Medica, *Centaurea behen* is also stated to contain this alkaloid bahamine, but no differentiation is made between the red and the white variety. On the other hand, Nadkarni refers to *Salvia haematodes* W., named 'behen' in Arabic, to contain the same alkaloid bahamine. The roots taken as a powder together with sugar allegedly cure jaundice and calculus affections, and are reported to be aphrodysiac.

Later on, the *Centaurea* species have been investigated by several workers. In 1940 Charaux and Rabate[1] reported that the fresh leaves of *C. scabiosa* contain 2% of a glucoside, the hydrolysis of which furnished glucuronic acid and a flavonol identified as scutellareol. Comparative studies showed the identity of this glucuronoside with scutellaroside. In the same year Dionis and Chermonaz[2] also detected alkaloids and glucosides in *C. diffusa* and *C. inuloides*, while *C. americana* contains, according to Moran, Briex and Couch,[3] 5.8 mg. free hydrogen cyanide per 100 g. of its seeds.

Neutral, acidic and alkaline aqueous extracts of *C. salmantica Linn.* were tested as blood sugar lowering agents. As a result an aqueous glycerol extract has been recommended orally in human diabetes by Aquilar and de Gregoria Rocansolano.[4] A crystalline unsaturated lactone, behenin, m.p. 79-80° C., tetrabromo derivative, m.p. 67° C., with the formulas $C_{24}H_{48}O_3$ and $C_{24}H_{48}Br_4O_3$, respectively, has been isolated from *C. behen Linn.* by Bhargava and Dutt.[5] Lofgren[6] isolated two carotinoid pigments from the stalks and leaves of *C. cyanus*. Bigorra, Lobo, Puig and Yufera[7] observed that aqueous extracts of several *Centaurea* species showed hypoglycemic action when injected intravenously. Numata detected ascorbic acid in several *Compositae* species. In *Centaurea* it varies from 3.2-91.5 mg. %. Finally in 1954 Zolotnitskaya[9] reported that all *Centaurea* species of Armenian flora give a general alkaloid reaction.

Through the courtesy of Hakim Mohammad Said of Hamdard Dawakhana, Karachi, fresh roots of white bahman were made available for the present investigation. It may be mentioned that they were found to contain an alkaloid, in contradiction to the report given in Pharmacographia Indica. The roots were cut into small pieces and extracted exhaustively with petroleum ether of b.p. 60-80° C. A fairly large amount of a slightly brownish, honey-like residue remained after removing the solvent and started depositing crystals on standing.

Notwithstanding these crystals, it was subjected to adsorption analysis on alumina (Brockmann, E. Merck) with petroleum ether, benzene and chloroform subsequently used as eluants. Preliminary tests made it feasible to combine the 95 fractions collected into 7 different groups.

Isolation of Taraxasterol Acetate.—The 4th group consisted of colourless crystals mixed with an oily material and was therefore investigated at first. Recrystallisation nine times from ethyl acetate furnished the pure substance showing the m. p. 249-50° C. and $[\alpha]^{27}_D = +99°$ in 1% cholorform solution. Analysis: C, 81.70; H, 11.15; O, 7.15; m.w. 428 (Rast, camphor). This would agree with a formula $C_{32}H_{52}O_2$, which requires C, 82.05; H, 11.11; O, 6.84. The infrared spectrogram (Fig. 1) showed a strong band between 1700 and 1800 $cm.^{-1}$ suggesting a carbonyl group, and another one at approximately 1250 $cm.^{-1}$ indicating a $-C-O$ bond. Neither aldehyde nor ketone reactions were positive, while at the other side the hydroxamic acid test was clearly positive. From these observations, an ester group was concluded. The substance furthermore must carry at least one double bond because acidified potassium permanganate was decolourised at once in the cold and bromine added in chloroform or carbon tetrachloride solution furnished a bromo derivative (melting at 211 °C.) from acetone.

In accordance with the suggestion of the presence of an ester group, hydrolysis with alcoholic alkali led to a colourless substance melting at 220 °C. from petroleum ether having still the

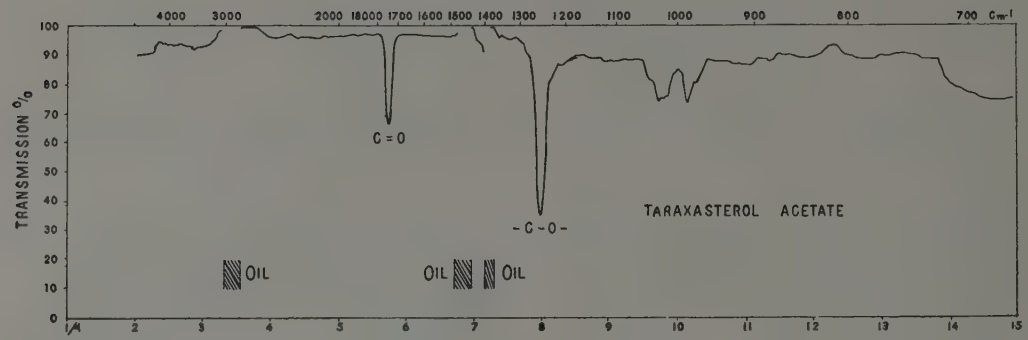


Fig. 1.—Infrared spectrogram of taraxasterol acetate.

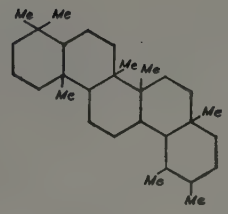
TABLE I

	m.p. °C.	Crystal structure	$[\alpha]_D$ 1% $CHCl_3$	Double bond reactions	Br. deriv. m.p. °C.	Liebermann test
Main subst. group 4	249–50	Colourless hexagon plates	+99°	Positive	211	Negative
Taraxasterol acetate	250–51	,,	+97°	,,	211	,,
Hydrolysate of subst. group 4	220	Colourless needles	+98°	,,	—	Positive
Taraxasterol	221–22	,,	+97°	,,	—	,,

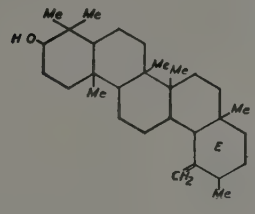
same rotation (namely $[\alpha]^{35}_D = +98°$ in 1% chloroform solution) as the starting ester. The analysis C, 84.67; H, 11.61; O, 3.92 would agree with $C_{30}H_{50}O$, which requires C, 84.5; H, 11.73; O, 3.76. The difference between the two formulas shows a loss of C_2H_2O, which indicates an acetate. This was confirmed by the determination of acetic acid by several methods described in the experimental part. The Liebermann-Burchardt test, negative with the original ester, was now positive, giving a change in colour from red to violet and then (after 1 day) into green. This is indicative of a hydroxy polycyclic compound. Consultation of Elseviers Encyclopaedia of Organic Chemistry leads to taraxasterol and its acetate, respectively. Table 1 shows the conformity of all the data.

Isolation of Taraxasterol.—Group 6 of the eluates was next taken up for purification. The colourless crystals of this group melted between 145-165°C., and could not be purified further by adsorption analysis on alumina. Recrystallisation was the only possibility, but, even after 20 recrystallisations from petroleum ether (alcohol and ethyl acetate, though furnishing much better shaped crystals, were less effective), the melting point, which had reached 217-18°C., was not yet constant. The rotation however ramained constant at $[\alpha]^{30}_D = +97°$ in 1% chloroform solution, which figure is identical with that of taraxasterol. An analysis of the material melting at 205-208°C. furnished C, 83.85; H, 11.61; O, 4.65 while taraxasterol $C_{30}H_{50}O$ requires: C, 84.5; H, 11.73; O, 3.67. The difference seems to indicate that the substance or substances that are connected with each other so obstinately in the product are not isomers. Taking into account the still rising melting point and the constancy of the rotation at the correct value, together with the fact that only taraxasterol besides its esters and ψ–taraxasterol (from group 1) could be isolated so far, it is reasonable to conclude that the main substance of group 6 is taraxasterol.

Jeger,[10] Lardelli,[11] and Dietrich[12] have shown that taraxasterol, ψ -taraxasterol, arnidiol and faradiol have the same skeleton as heterobetulin, which is obtained from betulin by isomerisation processes. All these compounds derive from the saturated hydrocarbon, heterolupane I.

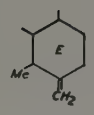


I



II

(a)
or



(b)

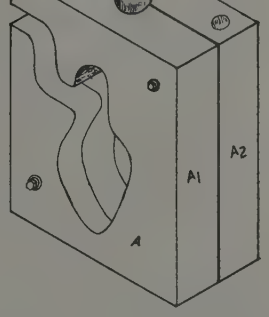
Taraxasterol II has been tentatively described to be 2,hydroxy Δ–19: 29 (a) or Δ–20:30 heterolupane (b). Taraxasterol occurs in the white rays of marguerite flowers also belonging to the same family *Compositae*. It was further isolated from the dried latex of *Lactuca virosa* and from *flos chamomilla romanae*, the flowers of *Anthemis bobilis*. In the latex of *Calotropis procera* (*Asclepiadaceae*), it occurs as acetate, isovalerate, pyroterebate, and probably other esters. It was futher isolated from the latex and the stem bark of *Centaurea gigantea*.

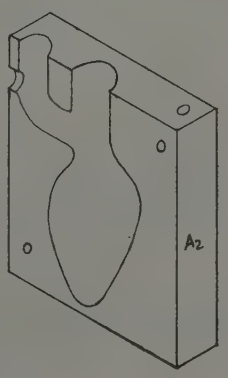
Isolation of the Myristic Ester of ψ-Taraxasterol.—The first group was received from the column as a water-clear colourless oil of high viscosity. It could be distilled in a copper block * at about 325 °C. 0.01 mm. Hg without colouration. Even the small amount of substance remaining in the distillation flask remained as colourless as before.

After standing for several months in air, the material became slightly yellow. The raw material was found to be neutral and free from fatty acids. The distillate on analysis gave the following values: C, 83.65; H, 11.89; O, 4.69. The infrared spectrogram (Fig. 3) showed a strong band between 1700 cm.$^{-1}$ and 1800 cm.$^{-1}$ suggestive of a carbonyl group, and another one at 1250 cm.$^{-1}$ indicative of a –C–O–bond. A small test confirmed that both groups are combined in an ester grouping. On saponification of the raw material with alcoholic alkali, a colourless crystalline substance could be obtained as the alcoholic part of the ester besides fatty acids. It was not possible to purify it by adsorption analysis, and it had to be recrystallised 15 times until the melting point was constant at 215-216°C. The rotation also was constant at $[\alpha]_D^{38} = +51°$ in 1% chloroform solution. It decolourises permanganate as well as bromine solution, and shows a series of transient colours with Liebermann-Burchard solution. Its analysis furnished: C, 84.6; H, 11.6; O, 3.8, in agreement with $C_{30}H_{50}O$, which requires: C, 84.5; H, 11.73; O, 3.76. On consulting Elseviers Encyclopaedia of Organic Chemistry the compound was found to be ψ–taraxasterol, which could be confirmed by preparing the acetate. Table 2 shows the conformity of the data.

ψ-Taraxasterol is known to occur always together with taraxasterol, from which it differs only in having the double bond within ring E, either between C 19:20 or 20:12. By refluxing taraxasterol with 10% alcoholic sulphuric acid in benzene for 5 hrs. it can be isomerised to ψ-taraxasterol.

Identification of the Fatty Acid with Myristic Acid $C_{14}H_{28}O_2$.—The melting point of the recrystallised fatty acid was found to be 47-49 °C. (from petroleum ether). Therefore both lauric acid (m.p. 43.6 °C.) and myristic acid (m.p. 54 °C.) had to be taken into consideration because





* For the distillation of very small amounts of substances, the apparatus shown in the figure has been developed and found to be very useful. The copper or brass block A is cut in two halves, A_1 and A_2, which can be put together by bolts. Inside the block, a recess is shaped to receive a small Claisen distillation flask of 2—10 ml. capacity with the capillary C and a short thermometer. An aperture of the same shape as the distillation flask in the front half of the block allows observation of the distillation. The copper block is heated by an open flame and provides uniform and constant heat up to that point where the vapours leave the distillation flask so that no overheating occurs.

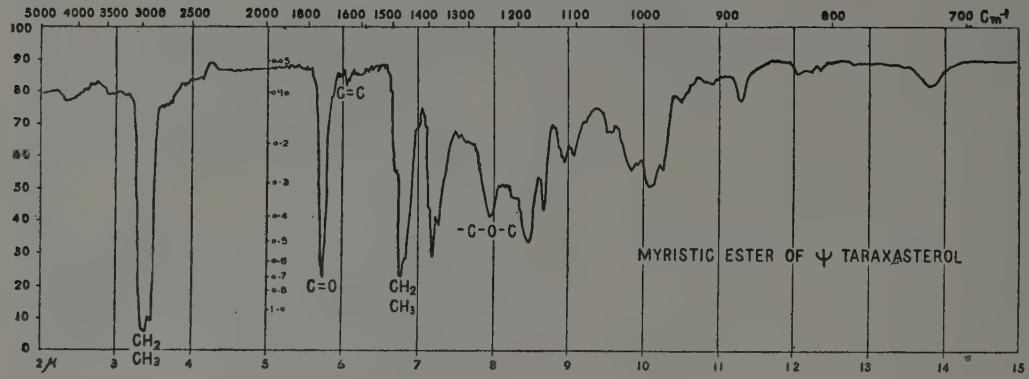


Fig. 2.—Infrared spectrogram of myristric ester of ψ-traxasterol.

TABLE 2

	m.p. °C.	Crystals	$[\alpha]_D$ 1% $CHCl_3$	Liebermann test	m.p. of acetate °C.
Hydrolysate of group 1	215–16	Needles	+51°	Positive	234–36
ψ – Taraxasterol	216–17	,,	+50°	,,	238

the iodine value of the raw acid was found to be 35 according to the method of Hanus, and furthermore the combined alcoholic solutions of the fatty acid and urea formed at once a nicely crystallised inclusion compound. From both observations it follows that the fatty acid must have a straight, unbranched, saturated chain. Assuming a single acid rather than a mixture, the melting point would favour myristic acid.

To make sure firstly that there is only one acid present, and secondly that it is myristic acid, the anilide has been prepared via the mixed anhydride of the fatty acid with phenylcarbaminic acid. This anilide was not only homogeneous, but showed also a melting point of 81-82° C. which agrees much more with that of myristic anilide (m.p. 81.5° C.) than with lauric anilide (m.p. 78° C.). The nitrogen values found are also in better agreement with the myristic anilide (N, 4.62; found, N, 4.7) than with lauric anilide (N, 5.02). The present authors therefore think that the main substance of group 1 is the myristic ester of ψ-taraxasterol. In the knowledge of the authors it has been found for the first time in nature.

Experimental

Extration with Pertoleum Ether.—Fresh roots of *Centaurea behen* (white variety) were cut into small pieces of 1/4″-1/2″ length and extracted three times with petroleum ether; b.p. 60-80° C.

Experiment I: 1.6 kg. roots, on extraction with 6 litres of petroleum ether, yielded 15.73 g. of solvent free extract (0.98% of the fresh roots or 1.1% of the dried roots, which contained 11% moisture).

Experiment II: 7 kg. fresh roots, on extraction with 20 litres of petroleum ether, yielded 56.5 g. extract (0.81% of the fresh and 0.93% of the dried roots, respectively, which contained 13% moisture).

Adsorption Analysis on Alumina (Brockmann, E. Merck).—*Experiment I:* 15.5 g. of the brownish, sticky mass was dissolved in a minimum quantity of petroleum ether and placed on top of a column of 50 cm. length, 4 cm. width, filled with 480 g. of alumina. As eluants, petroleum ether, benzene and chloroform were used successively. Ninety five fractions of 50 ml. each were collected. Total eluates received, 12.826 g.; remained in the column, 2.674 g.; total, 15.5 g.

Experiment II: 55 g. extract. Column had 4 cm. width, 90 cm. length and was filled with 800 g. of alumina. Fifty eight fractions of 50 ml. each were collected. Total eluates received, 47.637 g.; remained in the column, 7.363 g.; total 55.0 g.

On the basis of the physical appearance, solubility tests and microscopic examination, the fractions have been divided into 7 groups. The percentage yield of fractions is given on the basis of dried roots.

GROUP 1: A colourless oily mass. Expt. I, Fr. 5-8 and 17-20, 4.712 g.(0.33%); Expt. II, Fr. 1-13, 28.112 g. (0.46%); total, 32.824 g.

GROUP 2: A gel-like colourless substance. Expt. I, Fr. 9-16, 2.567 g. (0.18%); Expt. II, Fr. 14-16, 1.231 g. (0.02%); total, 3.799 g.

GROUP 3: A mixture of an oily substance with some crystals. Expt. I, Fr. 21-27, 0.617 g. (0.043%); Expt. II, Fr. 17-20, 1.173 g. (0.019%); total, 1.790 g.

GROUP 4: Mainly a crtystalline colourless substance. Expt. I, Fr. 28-80, 2.201 g. (0.15%); Expt. II, Fr. 21-50, 5.574 g. (0.092%); total, 7.775 g.

GROUP 5: An oily brownish substance. Expt.I, Fr. 81-92, 1.022 g. (0.07%); Expt. II, Fr. 51-53, 2.398 g. (0.039%); total, 3.420 g.

GROUP 6: Colourless needle shaped crystals. Expt. I, Fr. 93-94, 1.021 g. (0.07%); Expt. II, Fr. 54-56, 3.666 g. (0.06%); total, 4.687 g.

GROUP 7: A semisolid brownish mass with some crystals. Expt. I, Fr. 95, 0.449 g. (0.03%); Expt. II, Fr. 57-58, 2.156 g. (0. 03%); total, 2.605.

Isolation of Taraxasterol Acetate from Group 4.—The melting points of the several fractions from the first experiment are given in Table 3.

TABLE 3

Fr.	m.p.°C.	Fr.	m.p.°C.
28	150–195	58	214–219
33	190–216	63	215–220
38	211–216	68	217–220
43	212–218	80	219–221
53	212–218		

Fractions 58-80 were combined and recrystallised from ethyl acetate. After nine recrystallisations the m.p. remained constant at 249-50°C. The rotation in 1% chloroform solution was also constant at $[\alpha]^{27}_D = +98°$C. Found: C, 81.70; H, 11.15; O, 7.15. $C_{32}H_{52}O_2$ requires: C, 82.05; H, 11.11; O, 6.84. The infrared spectrogram is shown in Fig. 1.

Bromination.—100 mg. were dissolved in chloroform and a solution of bromine in chloroform was added dropwise until the colour persisted on standing for one hour. Solvent removed and recrystallised from acetone, m.p. 211°C. dec.

Hydrolysis to Taraxasterol and Acetic Acid.—200 mg. were refluxed with 40 mg. potassium hydroxide in 20 ml. of alcohol for about 9 hrs. The substance went slowly in a colourless solution. Concentrated to approximately half the volume, water was added to precipitate completely the fine colourless needles which already appeared on cooling. Yield, 180 mg., m.p. 210-213°C. They were easily soluble in chloroform, benzene, dioxane and tetrahydrofurane, sparingly so in ethyl acetate, petroleum ether, acetone and alcohol, insoluble in water. Recrystallised from petroleum ether m.p. 220°C. $[\alpha]^{35}_D = +98$ in 1% chloroform solution. Found: C, 84.67; H, 11.61; O, 3.92. Taraxasterol $C_{30}H_{50}O$ requires C, 84.5; H, 11.61; O, 3.92.

The alkaline mother liquor was brought to dryness (61 mg.) and submitted to spot tests for carboxylic acids (hydroxamic acid test), test for acetate, and finally for acetic acid itself according to Feigl. These tests were positive for acetic acid. Finally the rest of the salt was acidified and heated. The acetic acid could also be confirmed by the smell.

Isolation of Taraxasterol.—The colourless needle-shaped crystals of group 6 melted at 145-165°C. They were easily soluble in chloroform, benzene, dioxane and tetrahydrofurane; sparingly so in ethyl alcohol, methyl ethyl ketone, acetone, petroleum ether, ethyl acetate, cyclohexane and glacial acetic acid, insoluble in water. The purification was done by recrystallisation from several different solvents, among which petroleum ether was found to be the most effective, although the crystals from ethyl acetate or alcohol were much better shaped. Adsorption analysis on alumina failed to separate the mixture. Table 4 shows the slow rise in melting point for the successive recrystallisations.

The rotation obtained for No. 11 was $[\alpha]^{30}_D = +97°$ in 1% chloroform solution. With the Liebermann-Burchardt solution, the product gave a pink colour, which deepened slowly to purple and changed through violet and pale blue to light green during the next few hours. Potassium permanganate and bromine solutions were decolourised in the cold. Though all these data agree with taraxasterol, an analysis done with No. 11 (Table 5) showed a remarkable difference especially in the oxygen value and somewhat

TABLE 4

Recryst. No.	m.p.°C	Solvent
1	165– 77	Petroleum ether
2	178– 84	Ethyl acetate
3	184– 92	Petroleum ether
4	189– 97	,,
5	192– 98	,,
6	193– 98	Alcohol
7	195–200	Petroleum ether
8	197–202	,,
9	199–203	,,
10	203–207	,,
11	205–209	,,
after 19	215–217	,,
20	217–218	,,
21	217–218	,,

less in the carbon content, thus making it doubtful that the substance connected so obstinately with taraxasterol could be an isomer.

Found: C, 83.85; H, 11.61; O, 4.65. Taraxasterol requires: C, 84.5; H, 11.73; O, 3.76.

Isolation of the Fatty Acid Ester (Myristic) of ψ-Taraxasterol.—The clear, colourless oily substance of group 1 was distilled under high vacuum. To prevent overheating, the copper block already described has been developed. The oil distilled at 325°C., 0.01 mm, the high vacuum being produced by using an oil pump as pre-vacuum to a mercury pump. It is remarkable that no colouration took place even in the small amount of residue in the distillation flask.

The distillate gave the following values on analysis: C, 83.65; H, 11.89; O, 4.69. ψ-Taraxasterol myristic ester $C_{44}H_{76}O_2$ requires: C, 82.95; H, 12.03; O, 5.02; while the corresponding lauric ester $C_{42}H_{72}O_2$ requires: C, 82.83; H, 11.92; O, 5.25.

Saponification of the Myristic Ester of ψ-Taraxasterol.—16 g. of the raw oily substance of group 1 was refluxed with 20 g. of potassium hydroxide in 110 ml. alcohol. The oil went slowly into solution, which became dark red. After 13 hrs. boiling, it was cooled down and a few ml. of water were added in order to precipitate completly the fine colourless needles which appeared on cooling. They were filtered by suction, washed with a few ml. of an alcohol-water mixture (1:1) and dried on a porous plate. Yield, 5.15 g., mp. 155-162°C.

The red alkaline mother liquor was concentrated to about one third of its volume, so that the whole of the alcohol was driven off. The remaining solution was acidified with hydrochloric acid and the material coming out was taken up exhaustively with petroleum ether. After washing and drying, the petroleum ether was removed. Residue, 10.02 g.

A reddish brown substance still floating in the solution was taken up with amyl alcohol and found to give 0.8 g. of a reddish brown solid material.

The above mentioned residue of 10.02 g. was found to contain alkali insoluble material. It was refluxed for 3 hrs. with 10 g. potassium hydroxide in 80 ml. of alcohol, the alcohol was removed and the residue exhaustively extracted with petroleum ether. On removing the petroleum ether from the washed and dried solution, 4.8 g. of unsaponifiable substance of a glassy, brittle consistency was obtained. The petroleum ether insoluble portion, the soap, was dissolved in water and acidified. The fatty acids obtained were taken up in petroleum ether and yielded 5.1 *g*.

Purification and Identification of ψ-Taraxasterol.—The above received 5.15 g. of a sterol was dissolved in petroleum ether and passed through a column of alumina. But the outcoming eluates with different solvents revealed that no clear separation could be achieved. The regained substance therefore was subjected to recrystallisation from alcohol and petroleum ether successively. Table 5 shows the results.

The rotation of the last two fractions was also constant and showed $[\alpha]^{38}_{D} = +51°$ in 1% chloroform solution. The analysis agreed with the formula $C_{30}H_{50}O$ which requires C, 84.5; H, 11.73; O, 3.76. Found: C, 84.6; H, 11.6; O, 3.8;

The needle shaped crystals also gave a series of transient colours with the mixture of concentrated sulphuric acid and acetic anhydride (Liebermann-Burchardt test) and decolourised bromine and permanganate solutions.

ψ-Taraxasterol Acetate.—100 mg. of the substance, m.p. 215–216°C., was refluxed with 2 ml. of acetic anhydride and two drops of pyridine for about 3 hrs. Water was added to the still hot solution and cooled. The outcoming crystals were filtered by suction and dried on a

TABLE 5

Recrystl. No.	m.p. °C.	Solvent
1	165– 72	Alcohol
2	180– 87	,,
3	186– 93	,,
4	188– 95	,,
5	193– 97	Petroleum ether
6	197–202	,,
7	200–204	,,
8	202–205	,,
9	204–207	,,
10	206–209	,,
11	209–212	,,
12	211–214	,,
13	213–215	,,
14	215–216	,,
15	215–216	,,

porous plate, m.p. 234-236 °C. (three times from ethyl acetate). The plates are easily soluble in chloroform and benzene ; moderately so in ethyl acetate, petroleum ether and alcohol ; insoluble in water. ψ-Taraxasterol acetate melts at 238°C.

Identification of the Fatty Acid with Myristic Acid.—On recrystallisation of a small amount of the above received 5.1 g. of fatty acids from petroleum ether, the melting point was found to be fairly sharp at 47-49 °C.

The iodine value of the raw material to be determined according to the method of Hanus was found to be 35. The acid therefore must be a saturated one.

The combined solutions of the fatty acid and urea in alcohol form at once a nicely crystallising inclusion compound. It follows that the chain of the fatty acid must be a straight one. The melting point of lauric acid is 43.6 °C. while myristic acid melts at 54 °C.

Preparation of the Anilide.—2.4 g. of the dry fatty acid (raw material) was melted, 1.5 ml. phenyl isocyanate added and mixed by shaking in a round bottom flask closed with a calcium chloride tube by ground glass joint. Notwithstanding the outcoming crystals of the mixed anhydride of fatty acid with phenyl carbaminic acid, the mixture was heated in a glycerine bath until the effervescence stopped. The excess of phenyl isocyanate was then removed by using vacuum at 110-120°C. for approximately 1 hr. Afterwards the solidified anilide was pressed on a porous plate. Yield, 2.8 g. On recrystallisation from alcohol-water it turned out that all fractions melted sharply at 81-82°C. It follows that there is only one fatty acid present. The melting points of the anilides of lauric and myristic are 78 °C. and 81.5°C. respectively. Finally the nitrogen value was determined and found to be 4.7. The nitrogen value of lauric anilide is 5.02 as against 4.62 for myristic anilide.

Taking into consideration that nitrogen values tend always to be on the high side, the value would rather agree with myristic anilide than with lauric anilide. The same conclusion can be drawn from the melting points of free fatty acid as well as of their anilides. The present authors therefore think that the main substance of group 1 is the myristic ester of ψ-taraxasterol.

Acknowledgement

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UREA COMPLEXES: PREPARATION AND PURIFICATION OF ELAIDIC ACID, AND ITS GLYCERIDE ESTERS

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The technique of urea complex formation was first employed by Schlenk and Holman[1] for the separation of saturated fatty acids from the unsaturated. They also demonstrated easy urea complex formation by elaidic acid in comparison to its corresponding *cis* isomer, oleic acid. Later, these procedures were used by other workers.[2-6] Khan[7-8] purified the unsaturated fatty acids with the ingenious application of multiple steps of fractionation through urea complexes. In a current investigation,[9] he has shown the reasons for preferential precipitation of elaidic acid over *cis*-oleic, as urea complex crystals.

In the present investigation, the conditions for elaidinization have been described for larger yields of elaidic acid. A new method has been developed that involves generation of nitrogen dioxide gas right inside the larger quantities of fatty acids by addition of potassium nitrite and nitric acid together. Such procedures have been found advantageous in many respects: (a) elimination of separate arrangements for generating nitrogen dioxide, (b) shorter duration of isomerization and (c) preparation of larger amounts of elaidic acid. The instrumental set-up is quite simple and the starting materials need not be very pure in such procedures.

The prospects of separating elaidic acid from the standard mixtures have now been established through urea complex formation. Such data indicated the trends of fractionation through urea complexes and subsequent isolation of particular fatty acid. The experiments showed that elaidic acid cannot be well separated from the acids, but when oleic acid has been added to such mixture, elaidic acid could be isolated together with oleic acid. The oleic acid with more affinity for elaidic helps urea complex formation away from the saturated acids. Such processes have been termed "amplified urea complex segregation", because a third agent accentuates the urea complex formation. The knowledge of amplified distillation[10] will clear the picture.[11] It is now obvious that in the presence of oleic acid, elaidic acid can be separated from mixtures containing the saturates through urea complex formation. Elaidic acid was thus prepared in a pure state from the isomerized reaction mixtures of original sesame oil acids. Elaidinization converts linoleic and linolenic acids into polymers.[12] Consequently, their presence in the starting materials within limits, does not hamper purification of elaidic acid. These findings allow preparation of elaidic acid in larger quantities from three grades of starting materials: (a) saturate-free sesame oil acids, (b) saturate-free sesame oil acids containing 6-14% linoleic acid and (c) sesame oil acids containing 3-9% linoleic acid. The saturate-free sample does not contain any detectable amounts of the saturated acids, while the (c) sample contains the saturates with the unsaturates cut down, as noted.

The recovery of elaidic acid from (a) and(b) products was 15.0% and 22.0%, respectively, in the carefully conducted experiments. The isomerized (c) acids, through amplified urea complex segregation, yielded 11.0% pure elaidic acid. One advantage with (c) is that it involved one clear-cut series of procedures at one stretch. The urea complex formation (Tables 1-3) has been found in all these experiments to remove elaidic acid more effectively than simple crystallization methods. The data in Table 1 relate to the points that elaidic acid can be concentrated by urea complexes and then isolated in pure form

TABLE 1.—STANDARD MIXTURES AND SEPARATION. ELAIDIC: OLEIC ACIDS=1:1.

Fractions	% of original mixture	Iodine number	*Trans* contents (I.R.) % in fractions
1	18.0	88.9	81.0
2	24.7	89.4	72.5
3	22.0	89.6	44.1
4	20.0	89.4	36.3
5	15.3	89.8	12.9

TABLE 2.—STANDARD MIXTURES AND SEPARATION. STEARIC : ELAIDIC ACIDS=1:2.

Fractions	% of original mixture	Iodine number	*Trans* contents (I.R.) % in fractions
1	15.0	33.5	29.5
2	37.0	58.0	61.3
3	32.0	78.2	80.4
4	16.0	77.5	76.5

TABLE 3.—STANDARD MIXTURES AND SEPARATION. STEARIC: ELAIDIC: OLEIC ACIDS=1:1:1.

Fractions	% of original mixture	Iodine number	*Trans* contents (I.R.) % in fractions	% pure elaidic acid, recovered
I	18.0	31.2	12.0	—
II	24.0	40.7	18.0	—
III	11.4	58.9	34.0	—
IV	10.7	78.6	45.0	—
V	25.6	86.2	51.0	98.5%
VI	10.3	88.5	42.0	100.0%

through crystallization in acetone (25% solution) due to differences in solubility. Table 2 indicates that elaidic acid cannot be separated from stearic, because of their similar properties and solubilities in acetone. Table 3 shows that elaidic and oleic acids precipitate out together in the last fractions as urea complexes, free of stearic acid as the unsaturation(I.N.) provides the clues. The fifth and sixth fractions (Table 3) yielded on crystallization 98.5 and 100.0% elaidic acid. These results on the fractionations of elaidic acid helped the development of the procedures, "amplified urea complex segregation" for facilitating isolation of elaidic acid from the saturates by addition of a known unsaturated acid.

The tri-elaidin from pure elaidic acid and other types of glycerides with different contents of elaidic acid were also obtained by interesterification with refined sesame oil.

Experimental

Preparation of Saturate-Free Sesame Oil Acids.—Sesame oil acids(500 g.) in the presence of 600 ml. methyl alcohol were freed of the saturates in three steps, using (a) 200 g., (b) 100 g. and (c) 100 g. of urea in succession. The filtrate from the last step was slowly cooled in a bottle-cooler, in order to obtain a crop of urea complex crystals (about 40-50 g.). After quick removal of crystals under cold conditions, the filtrate was freed of the solvent. The yields of residual saturate-free acids were in the range of 65-72% in several batches of preparation.

The acid samples were esterified to methyl esters and then subjected to acetone-permanganate oxidation.[13] The oxidized esters were taken up in petroleum ether, (b.p., 80-90°C., freed of the unsaturates by the methods of Cooper and Melville[14]) and passed through a column of alumina (2.0 cm. × 60.0 cm.). The alumina was prepared by treating with 2N hydrochloric acid, washing with water until neutral and finally with alcohol. The acitivation was done at 150°C. for 6 hrs. The column eluants, first with pretoleum ether and then with petroleum ether containing 1% ethyl ether, did not give any neutral saturated fatty acid esters, palmitic or stearic in origin. This means that the above samples contained only unsaturated acids that got cleaved by permanganate oxidation into lower monobasic and dibasic fragments absorbed strongly by the alumina column.

Preparation of Saturate-Free Sesame Oil Acids containing 6-14% Linoleic Acid.—The above saturate-free sesame-oil acids in alcohol were again subjected to urea complex formation with an additional amount of 300 ml. methyl alcohol in one step. About 750 g. of urea in this boiled mixture was thoroughly stirred with strong glass rod for half an hour. The urea complexes were freed of adhering liquids and washed thoroughly with mixed (ether+petroleum, 1:1) solvent. The complexes gave the required acids with yields of 42-54% of the original sesame oil acids. The saturate-contents were checked as in the foregoing section. The linoleic acid contents were roughly determined by the bromide number methods with the relevant correction.[15]

Preparation of Sesame Oil Acids containing 3-9% Linoleic Acid.—Five hundred grams of sesame oil acids and 1 litre of methyl alcohol were boiled together and thoroughly stirred with 1200 g. of urea for over 30 minutes. The rest of the procedures were same as in the last preparation. The yields were in the range, 45-57%. The linoleic acid contents were checked through the procedures[15] mentioned above.

Preparation of Elaidic Acid in Large Quantities.—Several types of elaidinization reactions were carried out. (i) Nitrogen oxide gases were passed through 500 g. of crude sesame oil acids contained in a cylinder and agitated by air without any success. (ii) In another attempt, the oxides of nitrogen were mixed with oxygen in a tower filled with glass wool and were then passed through fatty acids with slightly better isomerizaton. (iii) The solid surface was considered necessary for *cis-trans* interconversion. However, the added pumice stone and powder gave unexpectedly low isomerization. (iv) The last and successful attempt was to use potassium nitrite and other salts formed from it as solid surfaces. Hence, the successful process of preparation was accomplished after a series of reactions by generating nitrogen oxides in the presence of oxygen with all reagents manipulated properly in the medium of fatty acids, as noted below.

Five hundred grams of sesame oil acids of grades (a) to (c) were successively placed in a cylindrical tube ($2\frac{1}{2}'' \times 20''$). Both potassium nitrite (140 g.) and concentrated nitric acid (60 ml.) were added in proportions to leave a slight excess of potassium nitrite in the mixture. The time of addition was between 10 to 15 min. Dried air was bubbled through the mixture during the addition and for 12 hours thereafter. In the last stages, precaution was taken not to stir the accumulated salts in the bottom of the tube too vigorously . The reaction mixture was left open to air in layers in glass trays for another 12 hours in a hood, and then washed into a 5-litre Florence flask with hot water. The wash liquid appearing as the bottom layer was siphoned off. After three washings, the residue was dissolved in petroleum ether (25-30% solution), left over anhydrous sodium sulphate for 24 hours and then filtered. One crystallization from the above solution, followed by several crystallizations (about 4 times) from acetone solution (30-40%) below 0°C., gave white crystalline products (yields in the range of 11-22%). Some solid acids were also recovered from the filtrates. The elaidic acid samples except from (c) batch were distilled under vacuum and subjected to physical and chemical analysis. Elaidic acid in one characteristic sample had the following properties: I.N. (iodine number), 89.4; n.e. (neutral equivalent), 282.4; nitrogen, 0.0%; C, 76.36; H, 11.82. Calculated for $C_{18}H_{34}O_2$: C, 76.59; H,12.05. Usually, elaidic acid samples had I.N. in the range of 88.9-89.6 and nitrogen 0.0%, indicating reasonable degrees of purity.

From the above crystallizations, the final filtrates were freed from the solvent. The unreacted oleic acid plus some elaidic acid were recovered from the filtrate residues of all batches through urea-inclusion compounds, since the polymers were unaffected by such treatment. The monomer portion of these residual acids was separated in seven fractions. One thousand grams of the acids (approx.) from different batches of experiments already described were mixed with 100 ml. of methyl alcohol and added to the boiling methyl alcohol (1 litre) containing 300 g. of urea. The mixture was well stirred during addition and overnight. The crystals were filtered, washed with ethyl ether and freed of the solvent. Six more fractions of crystals of urea-inclusion compounds were obtained by adding first II, 400 g. of urea to the above filtrate mildly boiling, and then III, 500; IV, 500; V, 400; VII, 200 g. of urea to the successive boiling filtrates from the similar crystallization processes in each fraction. The fractions of crystals were combined, freed from the urea by water, saponified and hydrolyzed in order to reconvert certain esterified portions to free acids. These acids were recycled for isomerization.

The (c) batches of sesame oil acids, containing saturated and 3-9% lionleic acids, gave fractions of elaidic acid contaminated by saturated acids through the above procedures of crystallization. A novel approach somewhat different from previous procedures,[1-5] has been made to isolate elaidic acid from the saturates by obtaining data on the degrees of separation in the standard mixtures during urea complex formation: elaidic acid (150 g.) and oleic acid (150 g.)-Table 1; elaidic acid (200 g.) and stearic acid (100 g.)-Table 2; elaidic acid (100 g.), stearic acid (100 g.) and oleic acid (100 g.)-Table 3.

The alcohol and urea used in each fractionation are: first mixtures, 600 ml. methyl alcohol; (1) 300, (2) 350, (3) 250, (4) 250 and (5) 200 g. of urea; second mixtures, 800 ml. methyl alcohol; (1) 250, (2) 450, (3) 350 and (4) 250 g. of urea; third mixtures, 500 ml. methyl alcohol; I, 200; II, 150; III, 200; IV, 200; V, 250; and VI, 200 g. of urea. Chemical and physical analyses were carried out for characterizing the fractions. The unsaturate-free stearic acid was obtained by only one course of hydrogenation, as described by the method of Khan.[16]

The valuable information available from the elaidic acid fractionations through urea complexes gave the clues to the new methods of elaidic acid separation. This has been accomplished by the addition of the unsaturated acids to the samples of elaidic acid contaminated with the saturates. Elaidic acid with saturates from (c) batch was mixed with oleic acid in the same amounts as those of elaidic acid in the sample and subjected to urea complex formation with successful results. The greater portion of elaidic acid came together with oleic acid fraction. Since 300 g. of the mixture was taken, the other reagents did not vary from the third standard mixture. The added substance, oleic acid, was removed in the filtrate by crystallization, while elaidic acid crystals easily separated out. This process may be given the name "amplified urea complex segregation" (AUS).

Preparation of Tri-elaidin and Mixed Trans-glycerides.—Elaidic acid (300 g.) was esterified with 95% glycerol (34 g.) in the presence of $SnCl_2,2H_2O$ (0.5 g.) at 200°C. under 20 mm. of mercury for 6 hours. Such reaction was carried out in 0.5-litre 3-necked flask with standard joints and the outlet for a long stem thermometer (standard joint) of 0°-250°C. The

low pressure was obtained by means of a vacuum pump with two traps, one 1-litre filtering flask in chipped ice and the other in the freezing mixture. A glass stirrer with a ground glass vacuum seal and a 20/40 joint was used for agitation. The reaction mixtures were refined according to the A.O.C.S. official methods[17] and tri-elaidin was recovered (yield, approx. 95-97%).

The refined[17] sesame oil was mixed with tri-elaidin in the proportions 65:35, and heated with sodium ethoxide (0.05%) as catalyst for interesterification at 180-200°C. under the atmosphere of hydrogen for 4 hours. The mixtures were then well washed and dried as a 30% solution in petroleum ether over anhydrous sodium sulphate. The mixed *trans* glyceride with about 30-35% isolated *trans* double bonds (10.36 μ) was obtained. Elaidic acid of 70-78% purity was also used for the same preparation of mixed *trans* glycerides with due allowance for the other acids present. In the case of preparing the synthetic triglyceride with about 10% isolated *trans* double bonds, the proportions of refined sesame oil and elaidic acid were 90:10. There was no difference in rest of the procedures. Iodine number (I.N.) was determined by Hanus method.[18]

Spectrophotometric Analysis.—Infrared absorption analysis was performed with the Perkin Elmer instrument, Model 21. The base line technique in conjunction with the absorption of pure elaidic acid, and tri-elaidin was used to determine the percentage *trans* contents.[19] The test wave lengths were 9.0-12.0 (particularly, 10.36 μ) and the solvent used was carbon disulphide. The infrared analyses were carried out under the courtesy of the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, U.S.A.

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A SURVEY OF MEDICINAL PLANTS OF THE KARACHI AREA

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Under the present economic conditions of this country and in the interest of the general welfare of the people, all possible resources need to be fully exploited. In particular the growing interest in the pharmaceutical industries necessitates a comprehensive study of the crude drug resources of our country. An attempt is made in the present work to study the possibilities of the medicinal plants available in the area within a radius of about 20 miles around Karachi, bounded to the south and west by the sea coast, with Manghopir to the north and Landhi and Malir in the east. Many of the plants of this region are being locally used in the treatment of certain ailments. Some of these plants are found wild in the natural vegetation, and some as weeds in the cultivated fields.[1] Of these, a few have received world wide recognition as medicinal plants and references will be made to them in this discussion.

A. Waste Lands

The soil condition of the waste lands in this region is not uniform and therefore there is considerable variation in the natural vegetation of this region. At least three different types of soil conditions are apparent.

(i) **Sand Dunes of the Sea Coast.**—The vegetation in this area is typically xerophytic. Among the natural flora there are a good number of plants that are used by local country doctors for medicinal purposes. An important medicinal plant, *Citrullus colocynthis* (Indrain, Sindhi), a reputed purgative, grows in abundance and can be collected in sufficient quantities. As this is a very good sand dune binder, its artificial regeneration in this region can serve a dual purpose. At present the fruits are collected on a small scale by the local drug dealers and are sold unpeeled. The peeled fruit was described in the British Pharmacopoeia, 1948.

Another very common plant of this region, *Cressa critica*, is valued for its alterative, anthelmintic and stomachic properties. *Tamarix troupii* is yet another plant that has received recognition as a medicinal herb; the leaves, bark, fruits and galls are used for their astringent properties in intestinal disorders. *Capparis aphylla* (Kureer, Punjabi), a dominant species in desert areas, is a popular drug plant among the local hakims for its diaphoretic, laxative and anthelmintic properties. It is also said to be useful in curing cough and asthma.

(ii) **The Calcareous Hilly Tracts.**—This area covers the hillocks of North Nazimabad, Manghopir, Country Club Road and its adjacent localities. In this region are found two most important medicinal plants—*Acacia senegal* (Khair, Sindhi) and *Commiphora mukul* (Guggal, Sindhi) (*Balsamodendron mukul*). *Acacia senegal* is a recognised source of gum, which finds extensive use as an emulsifying agent. The gum is also used as a demulcent in medicine. *Commiphora mukul*, commonly known as myrrh, produces an important oleoresinous substance. It is mildly disinfectant and acts as a local stimulant of the mucous membranes. Tincture murrhae is a B.P. preparation and is commonly used in mouth washes.

Unfortunately, at present no gum or resin is being extracted from these two important plants and people in the drug industry seem to be unaware that they are available in our country. *Acacia senegal* is found in profusion by the sides of the Karachi-Hyderabad road beyond Landhi, but the distribution of *Commiphora mukul* seems to be limited and large scale commercial exploitation of this plant may not be very profitable for some time to come because of its scanty growth. Systematised cultivation and propagation of these two plants in this region is likely to yield good results. It may be noted that India has been successful in propagating *Commiphora mukul*, from which the oleoresin is being exported by her under the name of Indian myrrh.

Small quantities of *Cymbopogon jwarancusa* (rosha grass), used in perfumery, can also be collected from the hilly regions. The white latex obtained from *Euphorbia tirucalli* (Sair, Sindhi), common in this area, is often used for its carminative and purgative properties by the local people. It is also said to be useful in jaundice, cough and leprosy.

A few other plants, viz., *Periploca aphylla*, (Barraree, Urdu), *Zygophyllum simplex* (Aletthi, Sindhi) and *Cordia rothii* (Gondnee, Urdu) are valued for their various medicinal properties by the local hakims, but these properties have yet to be established on a scientific basis. The milky juice of *Periploca aphylla* is used for external application to tumours and swellings, and a decoction of the bark serves as a purgative. It is reported that the Arabs

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beat up the leaves and the seeds of *Zygophyllum simplex* in water and apply the infusion in ophthalmia and leucoma. The bark and seeds of *Cordia rothii* are said to be useful in the treatment of ringworm.

(**iii**) **Alluvial Tracts.**—This is a very widespread area covering the whole of fallow uncultivated land in the plain. That part, which has been brought under cultivation, is rich in a number of medicinal plants. *Asparagus demosus*, *Boerhaavia diffusa* (Shothagni, Sindhi), *Calotropis procera*, (Ak, Urdu), *Cassia angustifolia* (Senna, Urdu), *Cleome viscosa* (Hurhur, Urdu), *Gynandropsis pentaphylla* (Hool-Hool-Sufaid, Urdu), *Salvadora persica* (Peelo, Sindhi), *Solanum xanthocarpum* (Kateli), *Peganum harmala*, (Hurmur, Urdu), and *Withania somnifera* (Ashvagandha, Hindi) are most common in this area.

Among these plants, *Cassia angustifolia* (senna) offers great commercial possibilities. Both the leaves and the fruits (pods) are used for purgative and laxative purposes and are recognised by the B.P.[2] At present the total requirements for these two purposes are imported from outside. This plant is cultivated in some south Indian states and the drugs are exported by India under the name Tinnevally senna. The active principles of these drugs available locally should be compared with those of Tinnevally and with those produced in Egypt. The possibilities for commercial exploitation of other plants are limited, because at present these are being used only in the indigenous and Ayurvedic systems of medicine where they are of importance in the treatment of ailments.

In indigenous medicine, the fasciculated roots of *Asparagus demosus* are largely used as diuretic, aphrodisiac and antispasmodic. *Boerhaavia diffusa*, a noted drug in the Ayurveda, is used in a number of ailments. An infusion of the herb is regarded as a mild laxative. The root is used as diuretic, laxative, stomachic and diaphoretic. The juice of the leaves is said to be efficacious in liver complaints. A number of therapeutic properties are attributed to *Calotropis procera* in the indigenous system of medicine.[2,3] The bark is found useful in inflammatory swellings, in cough, asthma and rheumatic pains. The root is considered to be a good substitute for ipecacuanha in dysentery, and is used as diaphoretic, emetic and alterative. It is reported that the seeds of *Cleome viscosa* have carminative and anthelmintic properties and are used as vermifuge and sinapism. A decoction of the root of *Gynandropsis pentaphylla* is considered to be a mild febrifuge and effective in tumours, ulcers and pain. The expressed juice of the root is considered to be good as a local application in otalgia.[2,3] *Paganum harmala* is quite often found to possess anthelmintic properties; this is attributed to the two alkaloids harmaline and harmine obtained from the seeds.[2,3] A preparation of the powdered seeds mixed with mustard oil is used for killing vermin infesting the hair. In Persian works, the fruit of *Salvadora persica* is valued for its carminative and diuretic properties.[2,4] *Solanum xanthocarpum* is used by local hakims in a number of ailments; the roots are considered valuable as expectorant, diuretic, febrifuge, and anodyne. The stem, flowers and fruits are carminative. The root of *Withania somnifera* is commonly used as alterative or diuretic and in rheumatic affections. An alkaloid, somniferine, is obtained from the root.

B. Cultivated Areas

These areas are located in the Malir, Memongot and its adjacent localities. It seems that the edaphic conditions of this region are well suited for growing the castor oil plant (*Ricinus communis*), which is found not only in this region but also as a very common weed throughout the plains of West and East Pakistan. No systematic effort has so far been made for its cultivation, and at present the total requirements of this important oil are imported. The oil from the seeds is the most widely used among purgatives.

Aloe vera (Gaekwar, Urdu), a plant of North African origin, is found cultivated almost everywhere in graveyards and seems to have been naturalized successfully. If necessary protection is provided, its cultivation can be extended to the adjoining waste lands. There is no doubt that, in the waste land of this region, the possibility of developing this important medicinal plant is immense. The drug, which is the crystallized juice obtained from the cut leaves, is the basis of more than one popular brand of laxative pill.

Among the weeds of this area may be mentioned *Abutilon indicum* (Peeli booti, Punjabi), *Achyranthus aspera*, (Putkunda, Punjabi), *Argemone mexicana*, *Caesalpinia bonducella* (Gujga, Urdu), *Datura alba*, (Datura, Urdu), *Phyllanthus niruri* (Neruri, Hindi), *Portulaca oleracea* (Khoolfa, Urdu), which are at present only of local importance.

The importance of *Abutilon indicum* is due to the sedative and diuretic properties exhibited by its roots. A decoction of the leaves is used in chest affections and in bronchitis. *Achyranthus aspera* is said to be used as a laxative and stomachic. However, a decoction of the herb is found useful in dropsical affections and it is recognised as a medicinal plant due to the presence of an alkoloid (berberine) in the yellow glutinous juice. The juice

is diuretic and alterative and is also found useful in dropsy, jaundice and skin diseases. *Caesalpinia bonducella*, found as hedge in cultivated fields, is a popular drug plant. The seeds are used as antiperiodic, antipyretic, and as bitter tonic in the Ayurvedic system of medicine. *Datura alba* is an important medicinal plant, and the alkaloidal contents and its properties are said to be not inferior to the species recognised in the British Pharmacopoeia. The leaves and the seeds of *Datura stramonium* contain two important alkaloids, hyoscyamine and atropine. The dried leaves and stems are smoked as an antiperiodic in asthma and whooping cough. *Phyllanthus niruri* is found useful as astringent, diuretic, stomachic and laxative. It is also used in many intestinal diseases. Another weed *Portulaca oleracea* is valued by local hakims for its alterative and refrigerant properties. It is also recommended in diseases of the bladder, kidneys and liver.

Conclusion

From the above discussion it is clear that some medicinal plants of universal reputation are available in this region. It is therefore suggested that some efforts should be made on scientific lines for their exploitation. The possibilities of commercial exploitation regarding *Acacia*, *Aloe vera*, *Citrullus colocynthis* and *Commiphora mukul* are particularly very great. The other drugs, such as a *Boerhaavia diffusa*, *Calotropis procera*, *Cassia angustifolia*, *Caesalpinia bonducella* and *Withania somnifera*, which are at present used only by local hakims, as well as other drugs mentioned, may also be expected to yield good results on thorough investigation.

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INVESTIGATIONS ON THE BY-PRODUCTS OF THE RICE MILLING INDUSTRY

Part II.—Vitamin E Concentrate from Rice Polishings

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Preliminary examination of the various by-products of the rice milling industry, described in the previous communication,[1] has shown that fine 'kutti' (rice polishing) is richest in vitamin B complex, vitamin E and other nutrients. It yields about 10% of oil with a vitamin E content of 0.16% on the weight of oil, which compares favourably with other natural sources of vitamin E, e.g. corn, cottonseed, soy-bean and wheat germ oils, the tocopherol content of which ranges from 0.1 – 0.3%. Although wheat germ oil is regarded as the main source of vitamin E concentrates, occasional references[2, 3, 4] are to be found regarding the industrial utilisation of rice germ for the production of vitamin E enriched oil, which is finding increasing application as an antioxidant in food technology. It was therefore considered of importance to evolve a suitable method for the production of vitamin E concentrates from fine kutti.

Conventional methods for the preparation of low-potency vitamin E concentrates are based on saponification of the oil with subsequent extraction and concentration of the tocopherols in the unsaponifiable fraction, and they give approximately eight-fold concentration of the tocopherols in wheat germ oil.[5] Direct extraction of wheat germ with hot ethanol followed by low temperature treatment of the extract to freeze out the extracted liquid material, and removal of the solvent also yields a tocopherol-enriched oil.[6] In another method, adsorption chromatography [7,8,9] has been used for the large scale production of tocopherols, while trans-esterification of the rice germ oil with ethyl alcohol using sulphuric acid as a catalyst has been exploited to get 10% concentrates of vitamin E.[4,10] However, the most important industrial method for the concentration of vitamin E from natural oils is the short-path, high-vacuum, molecular distillation method.[2,3] In the present investigation a new method has been devised to prepare from kutti oil a ten-fold concentrate of vitamin E by a simple process based on the insolubility of the sodium soaps in acetone.

Method and Results

The oil, with a saponification value of 179 and an acidity of 60.3% as oleic acid, was extracted with petroleum ether (b. p.40° – 60 °C.) from fine kutti (procured from Abdullah Rice Milling Factory, Larkana, Sind). One hundred grams of this oil was taken up in 130 ml. of acetone, and to this was gradually added a concentrated aqueous solution of 13 g. of sodium hydroxide. The temperature of the mixture rose to about 40 °C., by the heat of reaction which resulted in the neutralization and partial saponification of the oil. Three hundred ml. of acetone was then added with constant stirring. Most of the sodium salts of the fatty acids were precipitated and removed by centrifuging. The precipitate was repeatedly washed with acetone and the washings added on to the acetone solution, which was then kept overnight at 0°C. whereby a further quantity of sodium salts was removed. The solvent was then distilled off and the residue, consisting of oil, unsaponifiable matter, residual soaps, excess alkali and traces

Table 1.—Recovery of Vitamin E with Different Solvents

Process		Starting material		Concentrate		Recovery of vitamin E %
		Wt. of oil	Potency of oil (1 %)	Weight (g)	Potency (% vitamin E)	
Acetone process	Ether	100	0.15	7.61	1.6	81
	Petroleum ether ..	100	0.15	6.60	1.3	57
Normal saponification process ..		100	0.15	9.67	1.1	71

of acetone was designated 'crude concentrate'.

In an effort to obtain the maximum possible extraction of vitamin E from the crude concentrate, a comparison of two possible solvents, ether and petroleum ether, was made under controlled conditions. The soaps and excess alkali were removed by repeated washings with water, the ethereal solution was dried over anhydrous sodium sulphate, and freed of the solvent, the last traces of it being removed in an atmosphere of nitrogen. The results obtained with ether and petroleum ether as solvents are compared in Table 1 with those from the normal hot saponification process.

The concentrate in each case was a dark yellow viscous oil at room temperature. The vitamin E content was estimated by the α,α-dipyridyl-ferric chloride method of Emmerie and Engel,[11] the intensity of the red colour produced being measured on a Hilger photoelecrtic colorimeter using Filter 52(520 mμ).

From the above data it is evident that ether is much more efficient as a solvent than petroleum ether for the recovery of vitamin E from the crude concentrate. It may be noted here that a great advantage of the acetone process described in this paper over the saponification-ether extraction method lies in the fact that all the free fatty acids and a major portion of the glycerides are removed without using higher temperatures, which affect the recovery of vitamin E. Moreover, the subsequent extraction of non-saponifiables and the unreacted oil proceeds more smoothly and requires much smaller quantities of ether, cutting down the manufacturing cost.

Acknowledgements

The authors wish to express their indebtedness to Dr. S. Mahdihassan, Head of the Biochemistry Division, Central Laboratories, for his kind help during the investigation, and to Messrs. Abdullah Rice Milling Factory, Larkana, Sind, for kindly supplying the fine kutti.

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SOME SPECIAL SERVICES OFFERED BY PANSDOC

D. Loman

Pakistan National Scientific and Technical Documentation Centre, Karachi

The Pakistan National Scientific and Technical Documentation Centre (Pansdoc for short) has now been in operation for a year and a half, and many of the readers of this Journal have already called upon its services, while many more are aware of the nature of these services, details of which have been distributed widely among the scientific and technical institutions in Pakistan. As an introduction to this discussion of some of the special services which are now being developed, it is thus only necessary briefly to summarize these basic services. They are:—

(*i*) *Document Procurement:* Pansdoc will, on request, provide a microfilm or photocopy of any published scientific or technical paper, on receipt of adequate bibliographical details.

(*ii*) *Bibliographies:* Pansdoc will, on request, compile a selected list of references to the published literature on any special subject in the field of science and technology

(*iii*) *Translations:* Pansdoc will, on request, provide an English translation of any scientific or technical paper.

Though there are many problems to be overcome before we can guarantee a rapid 100% service, especially in the field of translations, where a great deal of training is needed before staff are fully competent, nevertheless we have dealt satisfactorily with hundreds of requests, and feel justified in extending our scope to include some other interesting aspects of scientific documentation.

Russian Literature

Even in scientifically advanced countries such as the U.K. and the U.S.A. it has been recognised in the last few years that Russian scientific literature has not received the careful attention that it merits, because the scientists themselves are, with few exceptions, unable to read Russian, and translations from it are costly and time consuming. As a result of discussion and cooperation between various organizations in the U.K. and U.S.A., both official and private, arrangements have been established during the last few years whereby a number of the leading Russian scientific and technical journals are being translated completely and made available as independent publications, or "cover-to-cover translations". The subscriptions to these "cover-to-cover" translations are naturally higher than those to the original journals, but even so they are much more economical than translations made on an individual basis (in response to an isolated request) and there is a great overall economy in translating manpower. A list of Russian journals of which cover-to-cover translations are known to be in hand is given in the Appendix. Pansdoc has made a careful scrutiny of this list and has decided to subscribe immediately to several titles likely to be of particular interest to scientific workers in Pakistan. The special significance of this is that Pansdoc will be able at short notice to supply microfilms or photocopies of the papers in these journals, at a cost very much lower than that of individual translations.

Some issues of journals in the fields of Biochemistry, Experimental Biology and Medicine, Pharmacology and Toxicology, and Chemical Technology have already been received, and Pansdoc will on request supply lists of contents of these journals. Later, it may be possible for Pansdoc to issue a regular bulletin giving the contents lists of these cover-to-cover translations; this would depend both on the degree of interest shown by the scientific public in Pakistan and on the staff position at Pansdoc. Moreover, the number of the cover-to-cover translations to which Pansdoc subscribes may be increased, again depending on the demand for them.

Literature Exchanges

Of equal importance is the question of literature exchanges between specialised organizations in Pakistan and their corresponding organisations in other countries. As an instance in point, during a recent visit to New Zealand, the author stopped over at Sydney, Australia, and made a point of calling at the Scientific and Industrial Research Organization and the Agricultural Department. The information officers and librarians of these organisations were more than willing to send us their own publications and to help us to organise exchanges between appropriate institutions in their countries and in Pakistan, and within a few weeks the author received a letter from the Dept. of Agriculture in Sydney giving details about the Journals of the Australian Institute of Agricultural Science, Rural Research in C.S.I.R.O., and the Australian Journal of Agricultural Research.

While fully aware of the importance of Commonwealth contacts, Pansdoc does not restrict its efforts to this area. Because of its position as a centre of scientific documentation and its link through Unesco and other channels with libraries all over the world, Pansdoc has already been able to acquire material, in the form of reference works and specialised publications, from a number of countries. It will be possible to acquire much more of this material from abroad when Pansdoc is in a position to offer suitable Pakistani publications in exchange. A practical arrangement would be that organizations in Pakistan interested in acquiring reference literature from abroad, on exchange terms, should inform Pansdoc of their interests and state what publications they have available for the exchange.

One advantage to the Pakistani recipient of operating through Pansdoc in this way would be that, in cases where the incoming exchange publications are not in English, Pansdoc would undertake to translate their contents list before passing them on. Another advantage would be that Pansdoc would keep a check on the due arrival of the publications.

At least one Pakistani scientific organization is already alive to the advantages of using Pansdoc for such purposes, namely the Meteorological Department, which recently referred to Pansdoc an enquiry from the official Chinese Institute of Scientific Information, requesting just such facilities for arranging exchanges. A list of scientific and technical publications offered for exchange by the Chinese institutions is now available at Pansdoc and copies can be obtained on request. Pansdoc has also received direct enquiries from important libraries and documentation centres in various other countries, including the U.S.S.R., Czechoslovakia and Japan, regarding the possibilities of publications exchanges. Especially in view of the currency difficulties experienced by most of the scientific institutions in Pakistan, the exchange method is a most useful way of obtaining literature from abroad, and Pansdoc will do its utmost to further such exchanges.

Scientific Contacts

Allied to the question of receiving published literature from abroad is the problem of establishing and maintaining direct contact with organizations and individuals doing related work in other countries. Pansdoc is accumulating as many reference works as possible to provide information of this nature, and will be glad to deal with enquiries in this class.

Commonwealth Index of Translations

This card index, which constitutes a very large and valuable reference work comprising thousands of items, is compiled in London from details supplied by all the countries of the Commonwealth, and a copy of the whole index is likewise sent to every country of the Commonwealth. In the case of Pakistan, this index is now held at Pansdoc, where it will in due course be used to make a check whenever Pansdoc receives a request for a fresh translation. In this way it will be possible to avoid wasting time and labour on making a new translation when one is already available. Since the translations index covers the whole field of science, the references will also be useful in compiling bibliographies on special subjects. Pansdoc is trying to take full advantage of this particular activity in the sphere of Commonwealth cooperation, and is already contributing its quota of translations to the index.

Incidental Equipment

A number of microfilm readers, obtained by Pansdoc through Unesco, have been supplied on long loan to leading scientific institutions in Pakistan, where they are giving valuable service, as they enable the research workers to obtain their information from microfilms instead of full-size photocopies, and save a good deal of time and money. Pansdoc will be glad to give information regarding the supply of these or similar microfilm readers on request. In this connection, mention may also be made of facilities for the proper storage and filing of microfilms. For its own use and for demonstration purposes, Pansdoc has obtained convenient three-drawer filing cabinets to take the standard 9″ film strip. Information about these and alternative accommodation for microfilms will be supplied by Pansdoc on request.

In conclusion, some mention must be made of the problems encountered by Pansdoc in its endeavours to give the scientists of Pakistan the 100% documentation service they need. Although as an institution Pansdoc is still very young—it is barely a year and a half since it commenced operation—its staff is now well able to deal with all normal document procurement enquiries. The users of its services may, however, be reminded that they can save themselves and also Pansdoc considerable time and trouble by stating fully and accurately the details of the papers they require. In regard to translations, it may also be pointed out that due to shortage of personnel, it is not possible at present to meet the demands as expeditiously as one would like, but efforts are being made to improve

this position. Further, in case of translations from Japanese and other languages for which it is particularly difficult to obtain the services of translators, it may be stated that the cost of the translations will be very much higher than for the more usual languages, and it is expected that those interested in translations from these languages will be prepared to pay at a somewhat higer rate for them, which will in any case still be highly subsidised.

Appendix

List of "Cover-to-Cover" Translations of Russian Journals

(Journals marked with an asterisk are being subscribed to by Pansdoc; copies of contents lists will be supplied on request, and microfilms or photocopies of individual papers will be supplied at Pansdoc's usual rates.)

Automatic Welding
Automation and Remote Control
*Biochemistry
Biophysics
*Bulletin of Experimental Biology and Medicine
Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences
Bulletin of the Academy of Sciences of the USSR: Geophysics Series
Bulletin of the Academy of Sciences of the USSR: Physical Series
Cement
Colloid Journal (USSR)
*Doklady: Biological Sciences Sections
*Doklady: Botanical Sciences Sections
*Glass and Ceramics
Instrument Construction
Journal of Analytical Chemistry of the USSR
*Journal of Applied Chemistry of the USSR
Journal of General Chemistry of the USSR
*Journal of Microbiology, Epidemiology and Immunobiology
Machines and Tooling
Metallurgist
Microbiology
Pharmacology
*Pharmacology and Toxicology
Plant Physiology
Problems of Hematology and Blood Transfusion
Problems of Oncology
Problems of Virology
Proceedings of the Academy of Sciences of the USSR: Agrochemistry Section
Proceedings of the Academy of Science of the USSR: Applied Physics Section
Proceedings of the Academy of Sciences of the USSR: Biochemistry Section
*Proceedings of the Academy of Sciences of the USSR: Chemical Technology Section
Proceedings of the Academy of Sciences of the USSR: Chemistry Section
Proceedings of the Academy of Sciences of the USSR: Geochemistry Section
Proceedings of the Academy of Sciences of the USSR: Geological Sciences Section
Proceedings of the Academy of Sciences of the USSR: Physical Chemistry Section
Radio Engineering
Radio Engineering and Electronics
*Sechenov Physiological Journal of the USSR
*Soil Science
*Soviet Joufnal of Atomic Energy (Supplement of the Journal of Nuclear Energy)
Soviet Journal of Atomic Energy (Consultants Bureau Translation)
Soviet Physics — Acoustics
Soviet Physics — Doklady
Soviet Physics — JETP
Soviet Physics — Technical Physics

NOTES & NEWS

Hopkins Prize for Prof. A. Salam

Prof. Abdus Salam, the leading Pakistani nuclear scientist who is now professor of applied mathematics in the Imperial College of Science and Technology, London, has been awarded the Hopkins Prize of the Cambridge Philosophical Society for his contribution to the theory of non-conservation of parity in physics. Prof. Salam has received tributes from all over the world for his outstanding contributions in this field.

The Hopkins Prize has been awarded every three years since 1867 for work in mathematical-physical or related fields, and its first recipient was Sir G.G. Stokes. Prof. Powell, Sir John Cockcroft and the late Sir John Lennard-Jones are among the more recent recipients.

Scientific Society of Pakistan

The annual conference of the Scientific Society of Pakistan was inaugurated at Karachi on the 8th December 1958 by Mr. Habibur Rahman, Minister for Education, Information and Broadcasting.

In his inaugural address, Mr. Habibur Rahman exhorted Pakistani scientists to come forward to make positive and purposeful contributions in the realm of science which would enable this country to take its proper place in the comity of nations. He deprecated the tendency to recall with nostalgia the past achievements of Muslim scientists and said that it was useless to talk of how our forefathers had held up the light and showed the way when there was darkness around. He pointed out that science had since then made rapid strides in the advanced countries of the world, but unfortunately during the last eleven years there had been very little progress made by Pakistan in this field. He felt however that there was, no cause for despondency and hoped that, if Pakistani scientist applied themselves to the task of research with a will and a purpose, they would soon have positive achievements to their credit.

Dr. Raziuddin Siddiqi, the President of the Society, who presided over the conference, made the plea that the Government should select brilliant scientists and provide conditions under which they could devote their time and talents to the pursuit of scientific research in laboratories and libraries free from cares and worries. He emphasized the need for so developing the national language that all branches of education could be imparted through its medium.

In his annual report, Dr. Afzal Husain Qadri, the Secretary of the Society, disclosed that a bureau would be set up to bring the scientists and the industrialists closer with the aim of full utilization of the results of scientific research in the field of industries. He mentioned that the Society was publishing two journals, Jadeed Science (in Urdu) and the Scientist (in English).

In the evening session, the first Ibne Sina Lecture, sponsored by the Society, was delivered in Urdu on 'Matter and Energy' by Dr. Raziuddin Siddiqi. The lecture was presided over by Dr. Salimuzzaman Siddiqui, Director, Scientific and Industrial Research.

In his lecture, Dr. Raziuddin said that Urdu technical terms were no more difficult for the average Urdu knowing public than the English technical terms were for an average Englishman. He traced the history of the problem of matter and energy from the Greek time and described the most modern views that have led to the discovery of nuclear fission as a source of energy. Dr. Salimuzzaman Siddiqui, in his presidential remarks, pointed out that after hearing Dr. Raziuddin he felt convinced that expression in one's own language could certainly bring the goods home and it would be a real service if our sciences are developed in the national language.

During the session of the conference, a symposium on 'Teaching of Science' was held on the 13th December 1958 under the presidentship of Dr. Nazir Ahmad, Chairman, Atomic Energy Commission. Its proceedings were also conducted in Urdu.

Speaking on the occasion, Dr. Nazir Ahmad emphasized the importance of the teaching of science in our schools and colleges. He observed that for many generations our society had suffered from stagnation of thought, in which atmosphere new ideas had found it difficult to germinate, while

worn out superstitions had held the ground. This attitude, he said, could be radically altered by extensive teaching of science. He stressed the need for teaching of science in the mother tongue, and suggested the adoption of the Roman script to overcome the difficulty of technical terms.

Other speakers who took part in the symposium included Dr. Raziuddin Siddiqi, Mr. S.N. Naqvi, Dr. S.M. Karim, Dr. Surat Ali Khan, Prof. Q. M. Aslam, Dr. H. H. Bilgrami and Dr. Rahimullah Qurashi.

The College of Eastern Medicine

The College of Eastern Medicine, sponsored by the Hamdard Dawakhana Trust, was opened in Karachi on the 14th August 1958 by Miss Fatima Jinnah. This college is the first step towards the realisation of a project which aims at the establishment of a mush larger institute for a co-ordinated study of the Unani, Ayurvedic and Chinese systems and for their integration with the western system. Besides the present college, the institute will comprise a hospital, a clinic, an animal house, a herbarium, a library, a workshop and laboratories for research.

Speaking at the opening ceremony, Miss Jinnah said that the secret of the progress of a nation lay in getting spiritual inspiration from their educational and cultural inheritance and continuing the constructional struggle in accordance with their temperament and genius. She paid tribute to the management of the Hamdard Dawakhana Trust for establishing the college.

Earlier Hakim Mohammad Saeed, Chairman of the Trust, gave a detailed account of the health conditions prevailing in both the wings of the country, and called upon the practitioners in the ancient and modern methods of this science to remove their prejudices and pool their efforts in the common interest to solve the problems facing our people.

Decision on the Patentability of a Process of Defoliating Cotton Plant

Agricultural and horticultural operations are not patentable but it is still common for the patent offices to receive applications in this field. One such recent application was by American Chemical Paint Company which came up for decision before Mr. Justice Lloyd-Jacob of the Patents Appeal Tribunal in the United Kingdom.

This application related to the harvesting of cotton so as to obtain the raw cotton wholly or partially free from other matter. The applicants had found that a known compound 3-amino-1, 2, 4-triazole was a defoliant of exceptional utility in the treatment of cotton, and they sought protection for the use of the new and improved defoliant in the well known method of defoliating the cotton plant before harvesting. The claim objected to read as follows:—

"1. A process for obtaining raw cotton wholly or partially free from other matter characterised by the preliminary step of applying to the plant, before harvesting, the compound 3-amino-1, 2, 4-triazole in a concentration and amount sufficient to bring about defoliation".

The applicants submitted that the removal of contaminants from raw cotton whether performed by hand or machine, undoubtedly constituted a manner of manufacture. They argued that there were very many industrial processes which were devoted, in this way, to preparing a raw material for later manufacturing processes. The applicants further submitted that there were a number of cleansing processes performed on cotton, particularly in the ordinary cotton processing at the factory, and said that it clearly could not be relevant whether the pre-treatment was carried out at the factory or on the plantation.

Mr. Justice Lloyd-Jacob, while disallowing the application, observed as follows:

"In terms, this claim relates the application of the chemical to a process for obtaining uncontaminated raw cotton, but in truth the treatment in no wise affects the cotton but only the growing cotton plant in the sense of removing the leaves from the plant. It is aimed at preventing a source of contamination of the cotton from becoming effective and not at removing deleterious matter from contaminated cotton. This effectively destroys the argument from analogy wherein it was contended that, as the removal of contaminents from raw cotton, whether by hand or machine, is a manufacturing step commonly carried out in factories or the like, a similar step carried out on the plantation should be treated as part of the manufacturing process.

The end product of the applicants' process is a growing cotton plant the leaves of which have been stripped, and in which the cotton portion has been wholly unaffected by the treatment. It is neither more clean nor more dirty than it was before, but, because of the application of a method of cultivation to the plant, the material available

for harvesting is more satisfactory than it would otherwise be. No raw cotton has been obtained by the treatment and the applicants cannot be said to have devised any means of obtaining it. The step they characterise as constituting their contribution to the art is productive not of the material they specify but of conditions wherein that material may more usefully or profitably be cultivated."—[(1958) R.P.C. 47-50].

Forthcoming International Conferences

Symposium on Fluorine Chemistry; July 15-17, 1959; The University, Birmingham, England.

International Union of Geodesy and Geophysics. WMO Symposium on Radiation and Atmospheric Ozone; July 20-26, 1959; Oxford, England.

Translators. International Federation of Translators 3rd Congress; July 27 to August 4, 1959; Bad Godesberg, Germany.

21st International Congress of Physiological Sciences; August 9-15, 1959; Buenos Aires, Argentine.

Symposium on Therapeutics. Organised by the Italian Section of the International Union of Pure and Applied Chemistry (IUPAC); August 20-27, 1959; Gardone, Italy.

9th International Congress on the History of Science; August 30 to September 6, 1959; Barcelona and Madrid, Spain.

17th International Congress of Pure and Applied Chemistry; August 30 to September 6, 1959; Munich, Germany.

2nd International Congress on Air Pollution; September 6-10, 1959; New York, U.S.A.

Fiber Attraction and Bending, Symposium; September 9-11, 1959; Institute of Paper Chemistry, Appleton, Wis., U.S.A.

International Rubber Conference; November 8-13, 1959; Washington, D.C., U.S.A.

World Power Conference. Sectional Meeting; June 5-9, 1960; Madrid, Spain.

Powder Metallurgy; International Conference; June 13-15, 1960; New York, U.S.A.

1st International Congress of Endocrinology, July 18-23, 1960; Copenhagen, Denmark.

2nd International Congress of Catalysis; July 4-9, 1960; Paris, France.

26th International Congress against Alcoholism; July 31 to August 5, 1960; Stockholm, Sweden.

7th International Congress of Soil Science; August 15-20, 1960; Madison, Wis., U.S.A.

Fifth International Congress on Nutrition; September 1-7, 1960; Washington, D.C., U.S.A.

PATENT NEWS

Abridgements of Patents of Pakistan Council of Scientific and Industrial Research

A process for the simultaneous production of refined shark liver oil and vitamin A concentrates alongwith the recovery of other therapeutically active by-products. S. Mahdihassan, M. Moinuddin, S. Maqsood Ali and S. Abdul Haq. (Pakistan patent 107859, February 28, 1957; Australian patent 220215 April 9, 1957; British patent 810643, May 16, 1957; Indian patent 60156, April 9, 1957).—This Journal, **1**, 250 (1958).

An improved clay plaster and bricks. A.H. Chotani and M. Aslam. (Pakistan patent 108239, March 11, 1957)—Moist clay is mixed with bitumen solution in a mineral solvent.

A process for the production of cottonseed oil-based coating compositions. Salimuzzaman Siddiqui and M. Aslam. (Pakistan patent 108246, April 5, 1957; Australian patent 218208, April 8, 1957; British patent 813955, April 23, 1957; Indian patent 60100, April 3, 1957).—This Journal, **1**, 250 (1958).

Improvements in or relating to the manufacture of light weight concrete. M. M. Qurashi, A.H. Chotani, A.K.M. Ahsanullah and M. A. Choudhari. (Pakistan patent 107520, April 27, 1957; Indian patent 60369, April 30, 1957).—This Journal, **1**, 250 (1958).

An improved wood preservative. Salimuzzaman Siddiqui, M. Aslam and Ashhad Mehdi. (Pakistan patent 108270, April 27, 1957; Indian patent 60367, April 30, 1957).—This Journal, **1**, 250 (1958).

A process for the production of an air entraining agent for cellular concrete. Salimuzzaman Siddiqui, M. Aslam and S. Jamal Quadir. (Pakistan patent 108318, April 27, 1957; Indian patent 60368, April 30, 1957).—This Journal, **1**, 250 (1958).

Improvements in or relating to emulsion type mimeograph inks and a new stabiliser therefor. Salimuzzaman Siddiqui and M. Aslam. (Pakistan patent 108319, April 27, 1957; Canadian patent 734, 396, August 9, 1957; Indian patent 60366, April 30, 1957).—The ink comprises a pigment, a vehicle such as a mineral oil, a stabiliser for the dispersion of the pigment in the vehicle, a drier such as lead and cobalt naphthenates or rosinates, and an aqueous solution of an emulsifying agent selected from the group of polyhydroxy aliphatic compounds such as glycerol, and solutions of carbohydrates such as cane sugar or molasses.

A process for the modification of tannin extracts for the manufacture of writing inks. Salimuzzaman Siddiqui, G. Hahn and R. A. Siddiqui. (Pakistan patent 108274, May 18, 1957; Indian patent 60781, June 14, 1957).—Tannin containing materials like divi-divi pods, myrobalans, algarobilla and valonia are extracted with water and the extract is subjected to acid hydrolysis.

Improvements in or relating to petrol gas plants. A. H. Chotani and S. M. Ishaq Ali. (Pakistan patent 107505, May 29, 1957; Indian patent 60783, June 14, 1957).—This Journal, **1**, 249 (1958).

A process for the simultaneous production of refined shark liver oil and vitamin A concentrates alongwith the recovery of other therapeutically active by-products. Salimuzzaman Siddiqui, S. Mahdihassan S. Maqsood Ali and S. Abdul Haq. (Pakistan patent 108322, May, 29, 1957; Indian patent 60782, June 14, 1957).—The crude liver oil is extracted with an organic solvent such as ethyl alcohol, stearine is removed from the extracted oil, and the extracted oil is refined to obtain refined oil containing vitamin A; and on the other side the alcoholic extract of the oil is concentrated and saponified, and cholesterol is separated from the unsaponifiable matter recovered from the hydrolysate to yield vitamin A concentrate.

A process for the isolation of alkaloids and alkaloidal complexes from the Rauwolfia species of plants. Salimuzzaman Siddiqui. (Pakistan patent 108539, June 28, 1957; Belgian patent 566712, April 11, 1958; Indian patent 60994, July 3, 1957).—The process comprises the steps of percolating the plant material with ethanol or methanol; removing the solvent from the percolate; partitioning the semi-solid residue between water and ethyl acetate or any other non-miscible organic solvent with a similar range of solvent action; extracting the aqueous layer with a hydroxylic, partially miscible organic solvent preferably amyl alcohol;

and extracting the combined amyl alcohol layer with water whereby an alkaloidal complex named 'serpajmaline' is obtained from the aqueous extract on removal of the solvent; while on the other side on removing the solvent from the ethyl acetate layer and digesting the residue with petroleum ether, an alkaloidal complex named 'ajmalexine' is obtained in the form of a petroleum ether insoluble powder, and another alkaloidal complex named 'resajmaline', from the petroleum ether extract on removal of the solvent.

A pharmaceutical composition for the treatment of hypertension. SALIMUZZAMAN SIDDIQUI, R. DEININGER and M. Alauddin. (Pakistan patent 108540, June 28, 1957; Belgian patent 565811, March 18, 1958; Indian patent 60995, July 3, 1957).—The composition comprises serpajmaline together with a pharmaceutical adjuvant.

Improvements in or relating to a choola using firewood or cowdung cakes. Lt. Col. M. ISHAQ and C.K. ILAHI. (Pakistan patent 108527, May 19, 1958).—In a double-walled choola, the outer wall is perforated at the bottom, the inner wall is perforated all around, both the inner and outer walls are sealed together at the top leaving an air gap in between, and the double-walled casing thus constructed is placed over a base which is raised above the ground and is perforated in the centre.

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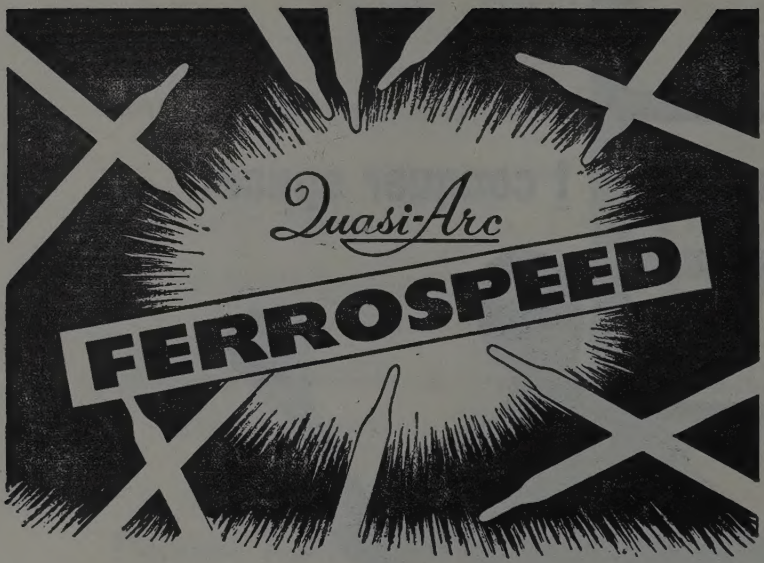

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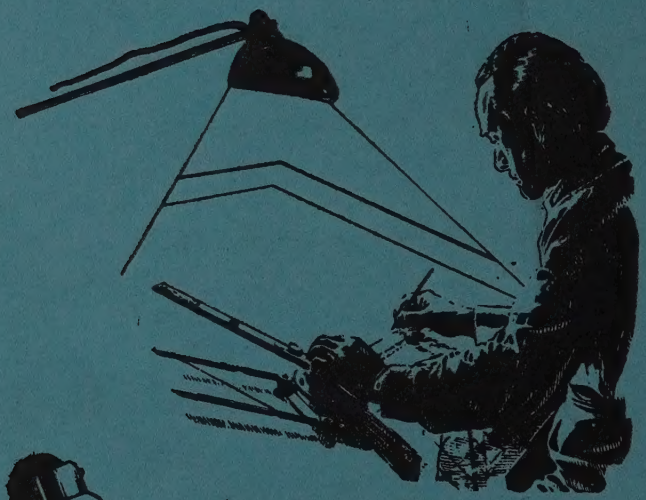

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